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Marion Le Gall, Sophie Ayrault, O. Evrard, Jean-Patrick Laceby, D. Gateuille, et al.. Investigating the metal contamination of sediment transported by the 2016 Seine River flood (Paris, France). *Environmental Pollution*, 2018, 240, pp.125-139. 10.1016/j.envpol.2018.04.082 . hal-01945405

HAL Id: hal-01945405

<https://hal.univ-smb.fr/hal-01945405>

Submitted on 16 May 2020

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Investigating the metal contamination of sediment transported by the 2016 Seine River flood (Paris, France)

Marion Le Gall^a, Sophie Ayrault^a, Olivier Evrard^a, J. Patrick Laceby^b, D. Gateuille^c, Irène Lefèvre^a,
Jean-Marie Mouchel^d, Michel Meybeck^d

^a *Laboratoire des Sciences du Climat et de l'Environnement, UMR 8212 (CEA/CNRS/UVSQ), Université Paris-Saclay, Domaine du CNRS, Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France*

^b *Environmental Monitoring and Science Division, Alberta Environment and Parks, 3115 – 12 Street NE Calgary, Alberta, Canada*

^c *Laboratoire de Chimie Moléculaire et Environnement, Université Savoie Mont-Blanc, 73376 Le Bourget du Lac Cedex, France*

^d *Milieux Environnementaux, Transferts et Interactions dans les hydrosystèmes et les Sols (UPMC/CNRS/EPHE), UMR 7619, Université Pierre et Marie Curie, 4 place de Jussieu, Paris Cedex, France*

Abstract

Fine sediment transport in rivers is exacerbated during flood events. These particles may convey various contaminants (i.e. metals, pathogens, industrial chemicals, etc.), and significantly impact water quality. The exceptional June 2016 flood of the Seine River (catchment area: 65 000 km², France), potentially mobilized and deposited contaminated materials throughout the Paris region. Flood sediment deposits (n=29) were collected along the Seine River and its main tributaries upstream (Yonne, Loing and Marne Rivers) and downstream of Paris (Oise and Eure Rivers). Fallout radionuclides (¹³⁷Cs, ⁷Be) were measured to characterize the sources of the material transiting the river, while trace elements (e.g. Cr, Ni, Zn, Cu, As, Cd, Sb, Pb, Tl, Ag) and stable lead isotopes (²⁰⁶Pb/²⁰⁷Pb) were analyzed to quantify the contamination of sediment transported during the flood. In upper sections of the Seine River, sediment mainly originated from the remobilization of particles with a well-balanced contribution of surface and subsurface sources. In the upstream tributaries, sediment almost exclusively originated from the remobilization of subsurface particles. In Paris and downstream of Paris, recently eroded particles and surface sources dominated the sediment, suggesting particles were mainly supplied by urban runoff and the erosion of agricultural soils. The highest metal concentrations and enrichment factors (EF) were found in the sediment collected in the Loing, Orge and Yvette upstream tributaries. Although these inputs were diluted in the Seine River, an increase in elemental concentrations was observed, progressing downstream through Paris. However, EFs in sediment collected along the Seine River were lower or in the same range of values sampled over the last several decades, reflecting the progressive decontamination of the urbanized Seine River basin.

Capsule

During the June 2016 flood of the Seine River there was a flush of contaminated sediment originating from upstream tributaries, while along the Seine River, sediment metal concentrations remained lower than historical records.

Keywords: Fallout radionuclides, trace elements, lead isotopes, fingerprinting

1 Introduction

Trace elements are naturally found in the environment, although at low background levels, as they are released by natural processes such as bedrock weathering or volcanic eruptions. However, anthropogenic activities may supply excessive quantities of metals and metalloids to the environment (Elbaz-Poulichet et al., 2001; Coynel et al., 2009; Resongles et al., 2014). In particular, large amounts of metals and metal compounds are released by industrial, domestic and agricultural activities (Suthar et al., 2009; Le Pape et al., 2012; Rosolen et al., 2015). In urbanized catchments, atmospheric fallout associated with anthropogenic activities provides one of the main pathways of soil contamination (Nriagu, 1989; Pacyna and Pacyna, 2001). Once emitted into the atmosphere, trace elements are transported and deposited through wet and dry fallout on soils where they may accumulate and be stored over long periods (Bindler et al., 2009; Bur et al., 2009). These hazardous compounds may be preferentially bound to fine particles (i.e. $<63\ \mu\text{m}$) (Blake et al., 2003; Owens et al., 2005) and they may subsequently be delivered to the riverine environment by processes such as soil leaching or soil erosion (Nystrand et al., 2012; Mileusnić et al., 2014; Zheng et al., 2016). The temporal dynamics of contaminants released by erosion processes are not well understood in urbanized catchments characterized by extensive impervious surfaces.

Although sediment and associated metals may accumulate in the river channel during low flow periods, they are mainly re-suspended and transported during flood events. Therefore, significant amounts of metals may be exported by rivers during very short periods (Cobelo-Garcia et al., 2004; Carter et al., 2006; Ollivier et al., 2011). Accordingly, the monitoring of flood events with high-temporal resolution sampling is essential to better understand trace element dynamics at the catchment scale (Cánovas et al., 2008). Studies based on robust flood monitoring remain scarce and, to the best of our knowledge, they were mainly restricted to small catchments impacted by former mining activities (Coynel et al., 2007; Turner et al., 2008; Resongles et al., 2015). The sampling of lag deposits may constitute an effective strategy to overcome the lack of sediment monitoring during extreme events (Lepage et al., 2016). Representative of the fine material transported by the flood and deposited during the falling limb (Olley et al., 2012), lag deposits are similar to fresh floodplain deposits originating from various catchment sources (Du Laing et al., 2009). Currently, there is a lack of data regarding the impact of flood events on water and sediment quality in large urbanized catchments (Baborowski and Einax, 2016). Furthermore, the determination of metal contents together with the identification and quantification of sediment sources during flood events are necessary for understanding their transfer at the catchment scale. Indeed, identifying both spatial and temporal sources of sediment is essential to interpret sediment

contamination levels and evaluate the resilience of major urbanized catchments. This important distinction may be resolved by combining several sediment source tracers (Bradley and Cox, 1990; Krüger et al., 2005).

Sediment sources may be identified by combining ^{137}Cs and ^7Be measurements. ^{137}Cs ($t_{1/2} = 30$ years) is an artificial radionuclide originating from thermonuclear tests (1950-1960s) and the Chernobyl accident in Northwestern Europe. Predominantly fixed to fine particles, ^{137}Cs discriminates between material eroded from the soil surface, exposed to atmospheric fallout, and from subsurface soils, sheltered from ^{137}Cs fallout (He and Walling, 1997; Motha et al., 2003). ^7Be ($t_{1/2} = 53$ days) is a short-lived cosmogenic radionuclide, supplied to the soil surface by precipitation, that discriminates between recently eroded particles, tagged with ^7Be and older re-suspended particles, depleted in ^7Be (Dominik et al., 1987; Taylor et al., 2013). Using these radionuclides, the relative contribution of four different sources (i.e. recently eroded surface and subsurface, re-suspended surface and subsurface) to sediment may be quantified and interpreted in terms of contamination levels using elemental concentrations (Evrard et al., 2016).

In this study, sediment sources and metal contamination levels were investigated during an exceptional flood event that occurred in June 2016 in the Seine River basin, France, representative of the industrialized areas of Northwestern Europe. This catchment, with approximately 16 million inhabitants, drains the Megacity of Paris and concentrates more than a third of the French heavy industries, leading to the coexistence of major anthropogenic pollution sources, including metal contamination (Meybeck et al., 2004; Grosbois et al., 2006; Thévenot et al., 2009). Although the June 2016 flood mainly affected the upstream tributaries with a return period > 50 years for the Loing tributary, the flood propagated along the Seine River with return periods estimated to be 10-20 years in Paris and 2-5 years in its downstream section near Poses. This flood was unprecedented, with the largest inundation in the Paris city center since the extreme flood event in 1910. In this context, stakeholder concerns arose regarding water quality, especially metal contamination. Furthermore, in the framework of the candidacy of Paris to host the 2024 Summer Olympics, the Seine River should be of sufficient water quality to hold the nautical competitions. The potential environmental impact of such major flood events needs to be investigated. Sediment metal contamination levels reached during this major flood need to be compared to historical data, and the sources of this contamination need to be investigated (i.e. contribution of recently eroded particle from impervious urban areas vs remobilized particles deposited on the riverbed during the last several decades). Accordingly, ^{137}Cs and ^7Be measurements were combined with the analysis of metal concentrations (Cr, Ni, Zn, Cu, As, Cd,

Sb, Pb, Ag, Tl) and stable lead isotopes ($^{207}\text{Pb}/^{206}\text{Pb}$) in lag deposits collected in the catchment to investigate the urban sediment contamination and the spatial and temporal variations of their sources during the June 2016 flood event in the Seine River basin, France. In addition, Predicted No Effect Concentrations (PNEC) were used to examine the potential toxicity of these contaminants on the environment.

2 Material and methods

2.1 Study area

The Seine River basin (65 000 km²) is located in Northern France and is characterized by homogeneous relief, geology and climate properties. The underlying bedrock is mainly sedimentary (~93%) with the predominance of carbonate rocks (chalk, limestone) while silicate rocks (7%) are restricted to the upstream Morvan area. Five main tributaries drain into the Seine River: the Aube (4750 km²), the Yonne (11 250 km²) and the Marne Rivers (13 160 km²) flow into the Seine upstream of Paris, whereas the Oise (16 900 km²) and the Eure Rivers (6017 km²) flow into the Seine downstream of Paris (Meybeck, 1998).

The land use is heterogeneous, with 25% of the catchment area dedicated to agricultural production and 40% to industrial activities. Agriculture is predominant upstream of Paris, whereas industrial activities are located near and downstream of Paris. With a mean population density of 250 inhabitants km⁻², varying from 15 inhabitants km⁻² in rural areas to a maximal value of 27 000 inhabitants km⁻² in the Paris conurbation, 23% of the French population lives in the Seine River catchment, which only covers 12% of the French surface area. The variations in land use, industrial activities and population density lead to variable anthropogenic pressures.

To investigate the spatial and temporal variations of metal contamination in sediment transported during the May 26 to June 4, 2016 flood event, attention focused on the flood sediment deposits collected along the Seine River (n=16) (from Bray-sur-Seine, upstream of the Yonne confluence, to Poses, the river mouth, 200 km downstream of Paris). Sediment deposits were also collected along the main tributaries (n=13), just before their junction with the Seine River: the Yonne, the Loing, the Orge, the Yvette and the Marne Rivers upstream of Paris and the Oise and the Eure Rivers downstream of Paris (Figure 1).

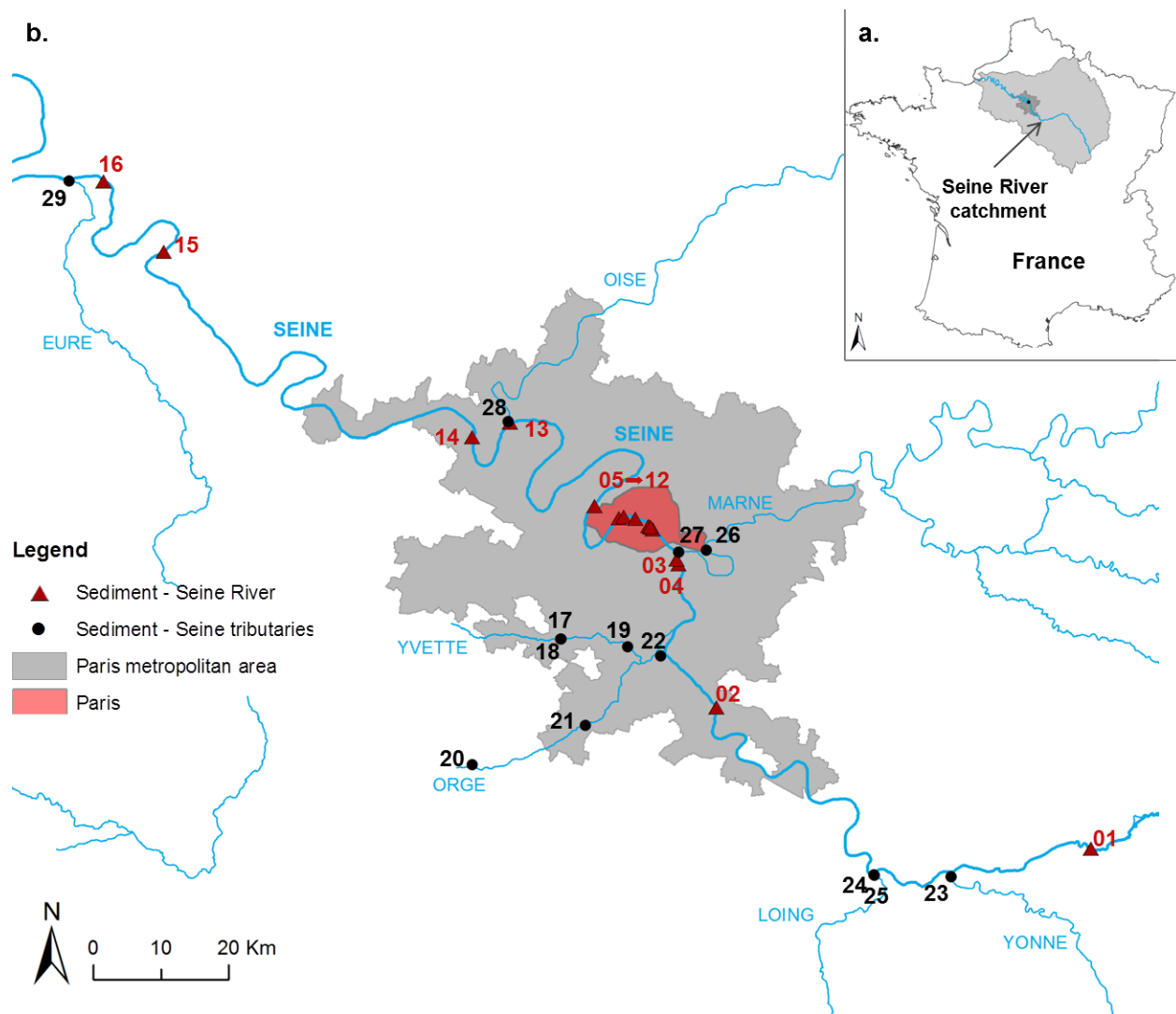


Figure 1. Map of the Seine River basin (France) (a) with the detailed map of the study area (b) and the location of the sediment samples collected along the Seine River (red) and its tributaries (in black).

2.2 Flood characteristics

From May 26 to June 4, 2016, a stationary low pressure system over France induced moderate although continuous rainfall during three days, from May 29 to May 31. This precipitation followed a particularly wet spring season. Soils were saturated and the additional rainfall first generated overflow of small rivers such as the Loing and Yvette. The upstream Loing tributary quickly reacted to heavy rainfall and several towns were flooded on June 1, with more than 4000 people evacuated in the city of Nemours. Although this catchment only covers 9% of the Seine River basin surface area, the Loing River contributed to 25% of the flood peak of the Seine River. The Yvette River, a small although highly urbanized tributary, also flooded several towns on June 2, with 2000 people evacuated in the town of Longjumeau. Characterized by return periods > 50 years, the flood of

these upstream tributaries propagated along the Seine River that reached its highest level on June 3 with a return period estimated to 10-20 years in Paris. However, flood impacts in Paris were less significant than in upper catchment areas and facilities vulnerable to flooding remained mainly unaffected (Van Oldenborgh et al., 2016).

2.3 Sampling and processing

Lag deposit sediment samples were collected following the flood of the Seine River. They were collected with a Teflon spatula to avoid any metallic contamination and oven-dried (~48 h) prior to analyses. Sediment samples were sieved to 2 mm for gamma spectrometry analyses and sieved to 63 µm for geochemical analyses.

2.4 Analyses

2.4.1 Radionuclide analyses

Fallout radionuclide activities (^{137}Cs , ^7Be in Bq kg^{-1}) were measured by gamma spectrometry at the Laboratoire des Sciences du Climat et de l'Environnement (Gif-sur-Yvette, France) following methods detailed by Gateuille et al. (2014). Between 50 and 80 g of sediment was analyzed, and measured activities were decay-corrected to the sampling date. Th concentrations (mg kg^{-1}) were estimated from ^{228}Th activities.

2.4.2 Geochemical analyses

Geochemical measurements were performed on mineralized sediment samples. Approximately 100 mg of sediment was successively dissolved by the addition of HF (4 mL, 47-51%), HClO_4 (2 mL, 65-71%), HCl (3.75 mL, 34-37%) and HNO_3 (67%, 1.25 mL) in closed Teflon vessel on hot-plates (Digiprep, SCP Science). Samples were cooled and evaporated to dryness between successive steps. Ultrapure reagents were used, a reference material (IAEA lake sediment SL1) and a chemical blank were digested in the same way as the sediment samples to control the mineralization efficiency and evaluate the potential contamination during digestion and analysis.

Elemental concentration and lead isotope measurements were performed in mineralized solutions using inductively coupled plasma mass spectrometry (ICP-MS, X Series, CCT II+ Thermoelectron, France). More details are provided in Le Gall et al. (2016) and Ayrault et al. (2012).

2.5 Modelling approach

The contribution of four distinct end-members was estimated in each sediment sample: re-suspended surface, re-suspended subsurface, recently eroded surface and recently eroded

subsurface. This approach incorporated both spatial and temporal sediment sources. To this end, surface sources were considered to be enriched in ^{137}Cs compared to subsurface sources, and recently eroded particles were considered to be labelled with ^7Be while re-suspended particles were depleted in ^7Be (Evrard et al., 2016).

A mixing model was used to determine the relative contribution of four distinct end-members to the flood sediment through simultaneously minimizing mixing model difference (MMD) using the solver function in Microsoft Excel:

$$MMD = \sum_{i=1}^n \left(ABS \left(C_i - \left(\sum_{s=1}^m P_s S_{si} \right) \right) / C_i \right) \quad \text{Eq. 1}$$

where n is the number of fallout radionuclides included in the model (i.e. 2); C_i is the activity of fallout radionuclide in sediment sample (i); m is the number of sources in the catchment (i.e. 4); P_s is the source (s) contribution to sediment; and S_{si} is the mean fallout radionuclide activity (i) in source (s). The proportional contribution from each source (P_s) was solved using the Solver function in Microsoft Excel with non-negative constraints and the contribution all of the sources summing to 1. Model uncertainty was summarized by adding and subtracting the analytical uncertainty to sediment samples and rerunning the models and then using the mean difference between the “+” and “-” uncertainty model runs to generalize model uncertainty.

The re-suspended surface ($n=64$) and subsurface ($n=8$) sources were respectively defined using soil (surface) and channel bank (subsurface) samples collected in upper parts of the Seine River catchment (Gateuille, 2013). The re-suspended surface end-member is enriched in ^{137}Cs compared to the re-suspended subsurface end-member and they are both depleted in ^7Be . The recently eroded surface end-member was characterized using overland flow samples ($n=6$) collected in a nearby cultivated catchment (see Le Gall et al. (2017) for more details). This end-member is defined by enriched ^7Be and ^{137}Cs activities. Finally, the recently eroded subsurface end-member was defined using urban runoff samples ($n=3$) collected in the Orge River, a subcatchment of the Seine River catchment, and is characterized by an enrichment in ^7Be and a depletion in ^{137}Cs activities (Froger et al., 2017). As particle size differences may prevent a direct comparison between potential sources and sediment (Lacey et al., 2017), a correcting factor based on thorium concentrations was used.

This particle size correction was shown to provide similar or even better results than a classical correction based on Specific Surface Area (SSA) (Foucher et al., 2015). Furthermore, as thorium

is measured by gamma spectrometry, no additional measurement is required. For these reasons, a thorium correcting factor was applied following the equation developed in Le Gall et al. (2016).

2.6 Statistical tests and Enrichments Factor (EF)

To investigate the correlation between the sediment elemental concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, statistical tests were performed using XLSTAT: 1) Spearman correlation coefficients were calculated for Th and major elemental concentrations and for the entire dataset normalized to Th and 2) a Principal Component Analysis (PCA) was conducted on the sediment dataset normalized to Th.

Enrichment Factors (EF), commonly used to evaluate the anthropogenic supply of an element in a given environment (Szuszkiewicz et al., 2016), were calculated as follows:

$$EF = \frac{(Me/Th)_{sample}}{(Me/Th)_{reference}} \quad \text{Eq. 2}$$

where $(Me/Th)_{sample}$ is the concentration ratio of the metal (Cr, Ni, Zn, Cu, As, Cd, Sb, Pb) to Th in each sediment sample and $(Me/Th)_{reference}$ the same ratio in the reference, corresponding in the current research to the geochemical background of the Seine River (Thévenot et al., 2007; Le Cloarec et al., 2011). This geochemical background was defined using fine sediment ($<100 \mu\text{m}$) at the Seine River mouth combining all the catchment lithologies. As Th is a conservative element that was shown to correct for the particle size effect in similar environments (Foucher et al., 2015), this element was preferred to using Al for EF calculations in this region.

3 Results

3.1 Radionuclide activities in sources and sediment samples

^{137}Cs and ^7Be measurements were combined to discriminate and model the contributions of four sources to the flood deposits: re-suspended surface, re-suspended subsurface, recently eroded surface and recently eroded subsurface (Figure 2, Table S1). For the re-suspended surface samples, ^{137}Cs activities ranged between $1.6 \pm 0.2 \text{ Bq kg}^{-1}$ and $53.1 \pm 0.7 \text{ Bq kg}^{-1}$ (mean 8.0 Bq kg^{-1} , standard deviation (SD) 0.1 Bq kg^{-1}) and between 0.0 ± 0.2 to $1.6 \pm 0.2 \text{ Bq kg}^{-1}$ (mean 0.4 Bq kg^{-1} , SD 0.3 Bq kg^{-1}) for re-suspended subsurface samples.

The recently eroded surface samples (i.e overland flow samples collected in a cultivated catchment) were characterized by ^{137}Cs activities varying from 3.1 ± 0.2 to $16.2 \pm 0.6 \text{ Bq kg}^{-1}$

(mean 4.7 Bq kg^{-1} , SD 4.7 Bq kg^{-1}) and the recently eroded subsurface samples (i.e urban runoff samples) by ^{137}Cs activities varying from 0.0 ± 0.3 to $1.2 \pm 0.4 \text{ Bq kg}^{-1}$ (mean 0.6 Bq kg^{-1} , SD 0.6 Bq kg^{-1}).

Flood sediment was characterized by ^{137}Cs activities varying from 0.0 ± 1 to $5.5 \pm 0.4 \text{ Bq kg}^{-1}$. The Th normalization was only applied to the re-suspended surface and subsurface end-members (i.e. soil and channel bank samples). Indeed, the other two end-members were defined by fine particle samples (i.e overland flow and urban runoff samples) and did not require a particle size correction as they were sediments and not soils. After normalization, activities in surface soil samples ranged between 3.6 ± 0.2 and $10.5 \pm 0.2 \text{ Bq kg}^{-1}$ and between 0.0 ± 0.5 and $0.7 \pm 0.1 \text{ Bq kg}^{-1}$ for channel bank samples, falling well within the range of ^{137}Cs values measured in sediment allowing a direct comparison with these samples.

^7Be activities in re-suspended sediment sources ranged between 0.0 ± 2.1 and $78.4 \pm 25.3 \text{ Bq kg}^{-1}$ (mean 4.2 Bq kg^{-1} , SD 17.1 Bq kg^{-1}) for soil samples and were null for channel bank samples. Recently eroded sources were characterized by ^7Be activities ranging between $98.6 \pm 4.5 \text{ Bq kg}^{-1}$ and $418.7 \pm 10.1 \text{ Bq kg}^{-1}$ (mean 232.1 Bq kg^{-1} , SD 145.6 Bq kg^{-1}) for overland flow samples and between 102.5 ± 7.4 and $412.3 \pm 29.8 \text{ Bq kg}^{-1}$ (mean 279.1 Bq kg^{-1} , SD 159.4 Bq kg^{-1}) for urban runoff samples. For sediment samples, ^7Be activities ranged between $0.0 \pm 9.6 \text{ Bq kg}^{-1}$ and $228.5 \pm 6.0 \text{ Bq kg}^{-1}$ and were in the range of variations of the sediment sources.

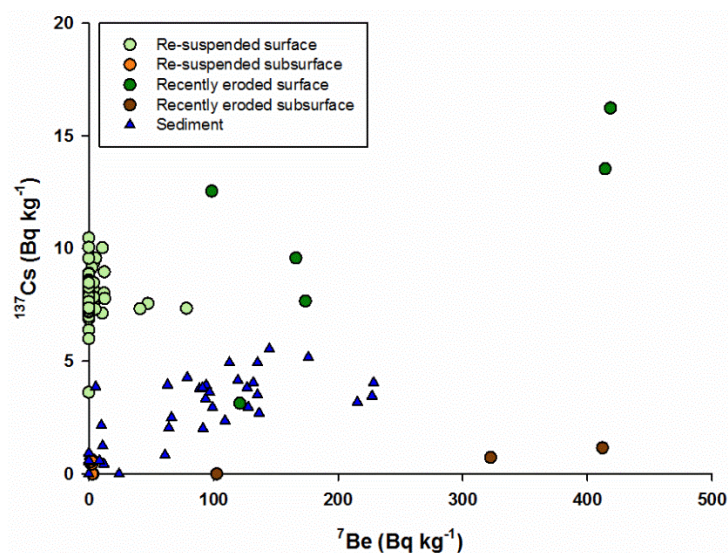


Figure 2. ^{137}Cs and ^7Be activities (Bq kg^{-1}) in the four source end-members (i.e re-suspended surface, re-suspended subsurface, recently eroded surface, recently eroded subsurface) and in sediment.

3.2 Modelling results

High variations were observed in the contribution of the four end-members to the sediment (Figure 3, Table S2). Upstream of Paris, subsurface sources largely dominated with contributions ranging between 50% (N°25) and 100% (22) with the exception of one sediment sample close to Paris (04) with a dominant surface contribution (88%) (Figure 3a, b). A mixing between recently eroded and re-suspended subsurface sediment was observed for the Yonne (23) and Loing (25) tributaries as for the Seine sediment samples (01, 02). Recently eroded subsurface contributions ranged between 17% and 32% and re-suspended subsurface contributions between 22% and 41%. In the Orge catchment, re-suspended subsurface contributions were the highest, with a mean contribution of $93 \pm 8\%$ for the Orge and Yvette sediment (17-22). For the Marne tributary, the contribution of the subsurface source dominated with a mean value of $70 \pm 13\%$. The uppermost Marne sediment sample (26) is characterized by a re-suspended particle contribution of 79% while for the sediment sampled just before the confluence between the Marne and the Seine Rivers (27), contributions of recently eroded and re-suspended particles as well as surface and subsurface particles were well-balanced, with respective contributions of 48% and 52% and of 40% and 60%. Overall, for the entire set of sediment collected upstream of Paris, subsurface material dominated although a very limited supply of recently eroded surface particles was observed, with contributions ranging between 0% and 19% with the exception of one sediment sample (04) with a contribution reaching 47%.

In Paris, sediment was dominated by the contribution of surface sources (mean value of $68 \pm 17\%$), especially recently eroded particles with a mean contribution of $48 \pm 14\%$. The re-suspended subsurface material contributed between 0% and 58% and the recently eroded subsurface contributions were the lowest with proportions between 1% and 13% (Figure 3b).

Downstream of Paris, only two sediment samples, collected in Conflans-St-Honorine (13) and Bouafle (15) exhibited high subsurface contributions (71% and 77%, respectively). In all other samples, recently eroded particles largely dominated with contributions varying between 74% and 96% corresponding to a clear dominance of surface particles with contributions between 51% and 84%. Sediment from the Eure (29) and Oise (28) tributaries exhibited the highest recently eroded surface contributions with respective values of 64% and 84%.

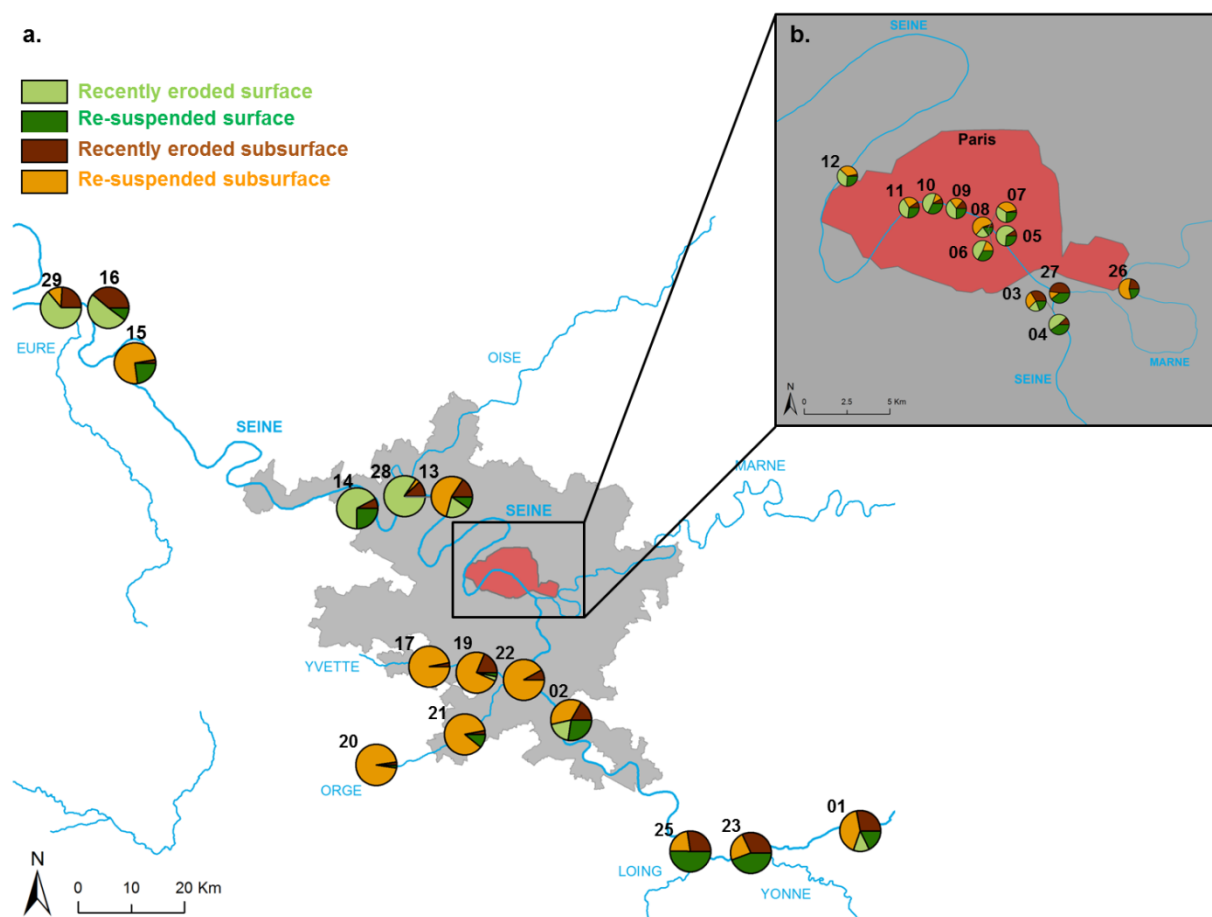


Figure 3. Spatial evolution of the contributions of the four end-members to the sediment collected along the Seine River and its tributaries.

3.3 Elemental concentrations, lead isotopes in sediment samples

3.3.1 Elemental concentrations

When considering the entire set of sediment samples collected along the Seine River, a global increase in metal and metalloid concentrations was observed in a downstream direction (Figure 4, Table S3 and Table S4 for major elements) with concentrations ranging between 29 and 83 mg kg⁻¹ for Cr, 15 and 34 mg kg⁻¹ for Ni, 69 and 402 mg kg⁻¹ for Zn, 14 and 90 mg kg⁻¹ for Cu, 3.2 and 11.3 mg kg⁻¹ for As, 0.3 and 1.9 mg kg⁻¹ for Cd, 0.4 and 3.2 mg kg⁻¹ for Sb, 15 and 214 mg kg⁻¹ for Pb, 0.1 and 3.95 mg kg⁻¹ for Ag, 0.26 and 0.90 mg kg⁻¹ for Tl. The lowest contents were systematically observed in the uppermost Seine River sample (01), with the exception of one sample in Paris (08), showing a slightly lower Ni content. An increase in As and Tl concentrations, with respective values of 7.4 to 12.7 mg kg⁻¹ and 0.46 to 0.87 mg kg⁻¹, was observed in sediment collected in Paris compared to the material sampled at both upstream and downstream locations. For the remaining elements (Cr, Ni, Zn, Cu, Sb, Pb), a slight increase was observed in sediment

collected in Paris (05-12), before decreasing in a downstream direction (13, 14). An increase in Ag content (maximal value of 3.95 mg kg^{-1}) was observed just downstream of Paris, and a continuous increase in Cd was observed all along the Seine River sediment. Importantly, sediment collected in Bouafle (15), downstream of the Seine River, was enriched in Cr, Ni, Zn, Cu, Cd, Pb with the highest concentrations measured in the current research.

The Yonne River sediment (23) exhibited much higher As (10.8 mg kg^{-1}) and TI (0.89 mg kg^{-1}) concentrations than the Seine River sediment collected before/after the confluence (01, 02, 03).

Sediment from the Loing River (24, 25) was particularly enriched in Zn ($165\text{--}300 \text{ mg kg}^{-1}$), Cu ($42\text{--}67 \text{ mg kg}^{-1}$), As ($10.2\text{--}11.3 \text{ mg kg}^{-1}$), Cd ($0.8\text{--}1.1 \text{ mg kg}^{-1}$), Sb ($1.6\text{--}2.6 \text{ mg kg}^{-1}$), Pb ($129\text{--}214 \text{ mg kg}^{-1}$), Ag ($0.20\text{--}0.63 \text{ mg kg}^{-1}$), with concentrations 3 to 14 times higher than those estimated in the Seine River sediment collected in upper catchment areas.

Concentrations in sediment from the Marne tributary (26, 27) were in the same range of variations than sediment collected just upstream and downstream of its confluence with the Seine River. Only TI concentrations ($0.31\text{--}0.38 \text{ mg kg}^{-1}$) were lower than in the Seine River sediment while one sediment sample (26) exhibited a notably high Cr concentration (83 mg kg^{-1}).

The Orge tributary sediment (20, 21, 22) exhibited lower Cr ($16\text{--}19 \text{ mg kg}^{-1}$), Ni ($8\text{--}9 \text{ mg kg}^{-1}$), As ($2.4\text{--}2.7 \text{ mg kg}^{-1}$), TI ($0.22\text{--}0.28 \text{ mg kg}^{-1}$) and similar Zn ($78\text{--}152 \text{ mg kg}^{-1}$), Cu ($15\text{--}28 \text{ mg kg}^{-1}$), Cd ($0.3\text{--}0.5 \text{ mg kg}^{-1}$), Sb ($0.7\text{--}1.1 \text{ mg kg}^{-1}$), Pb ($25\text{--}52 \text{ mg kg}^{-1}$), Ag ($0.07\text{--}0.46 \text{ mg kg}^{-1}$) concentrations compared to the sediment collected after its confluence with the Seine River.

The downstream Yvette sediment (19) systematically displayed higher concentrations than the upstream Yvette sediment (17, 18). Cr (55 mg kg^{-1}), Ni (21 mg kg^{-1}), As (7.3 mg kg^{-1}), and Cd (0.6 mg kg^{-1}) metal contents were similar to those of sediment collected in the Seine River downstream of the confluence while Zn (152 mg kg^{-1}), Cu (68 mg kg^{-1}), Sb (3.2 mg kg^{-1}), Pb (83 mg kg^{-1}) and Ag (0.89 mg kg^{-1}) contents were higher and TI (0.41 mg kg^{-1}) contents lower. For the remaining sediment (17, 18), their concentrations in Cr ($34\text{--}45 \text{ mg kg}^{-1}$), Ni ($12\text{--}19 \text{ mg kg}^{-1}$) were similar to those measured in downstream Seine River sediment while Zn ($92\text{--}121 \text{ mg kg}^{-1}$), Cu ($25\text{--}30 \text{ mg kg}^{-1}$), As ($4.1\text{--}4.5 \text{ mg kg}^{-1}$), Cd (0.3 mg kg^{-1}), Sb ($0.8\text{--}1.0 \text{ mg kg}^{-1}$), Pb ($37\text{--}40 \text{ mg kg}^{-1}$), Ag ($0.19\text{--}0.33 \text{ mg kg}^{-1}$) and TI ($0.27\text{--}0.30 \text{ mg kg}^{-1}$) were lower.

Downstream of Paris, the Oise tributary sediment (28) was characterized by the highest Cr (68 mg kg^{-1}) and Ni (31 mg kg^{-1}) concentrations although a lower Ag concentration (0.26 mg kg^{-1}) compared to downstream sediment of the Seine River. For the Eure tributary sediment (29),

357 elemental concentrations were similar to those of the nearest Seine River sediment (16), except
358 for Pb showing a maximal value of 156 mg kg⁻¹ and TI exhibiting a lower value of 0.35 mg kg⁻¹.

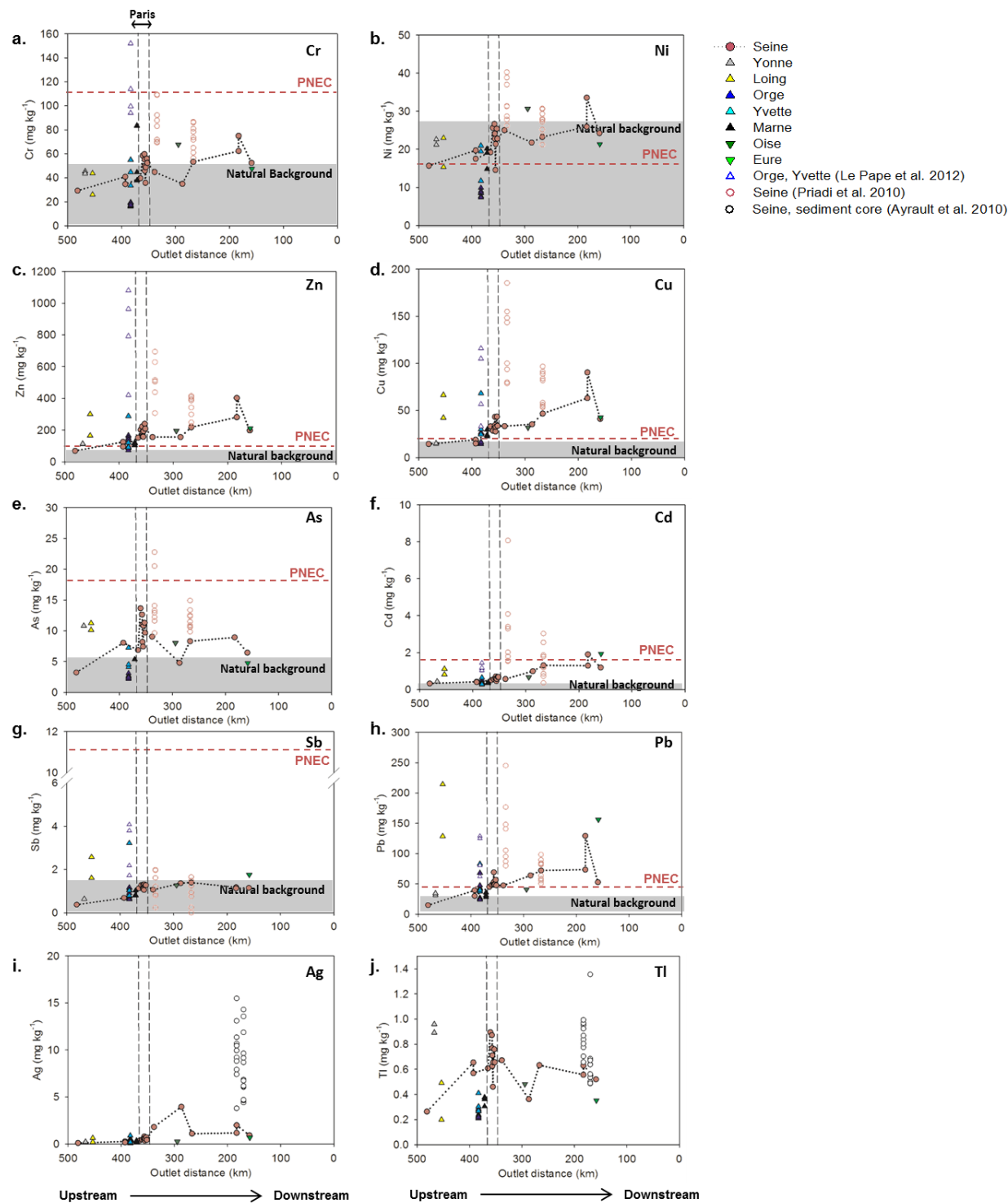


Figure 4. Spatial evolution of sediment trace element concentrations in the downstream direction along the Seine River. Circles with the dotted line corresponds to the Seine River samples and triangles to the tributary samples. Natural background and Predicted No Effect Concentrations (Barjhoux et al., 2016) for sediment are also presented.

3.3.2 Lead isotopes ratios

$^{206}\text{Pb}/^{207}\text{Pb}$ ratios measured in the Seine River sediment ranged between 1.1637 ± 0.0030 and 1.1847 ± 0.0051 . In sediment collected in tributaries, $^{206}\text{Pb}/^{207}\text{Pb}$ isotopes ranged between 1.1422 ± 0.0066 and 1.1838 ± 0.0014 (Figure 5, Table S3). Sediment from the Seine River was characterized by a decrease in Pb ratios associated with an increase in Pb concentrations in downstream direction. This reflects a change in sources, from the natural to the urban end-members. The urban end-member corresponds to the signature of the Pb emitted by a Parisian waste water treatment plant. This signature is interpreted as a mixing of historical Parisian lead with lead from gasoline (Ayrault et al., 2012). The sediment collected in the Yonne, Marne and Oise tributaries had higher $^{206}\text{Pb}/^{207}\text{Pb}$ and $1/\text{EF}$ ratios compared to the Seine River sediment with ratios varying from 1.1728 ± 0.0024 in the Marne sediment (26) to 1.1838 ± 0.0014 in the Yonne sediment (23). To the contrary, sediment from the Orge, Yvette, Loing and Eure tributaries was characterized by lower Pb isotopic ratios ranging between 1.1422 ± 0.0066 for the Eure sediment (29) and 1.1744 ± 0.0053 for the Orge sediment (17). Sediment plotted well between the natural and urban end-members, with the exception of the Eure sediment (29), showing the lowest Pb ratio and likely impacted by the leaded gasoline end-member.

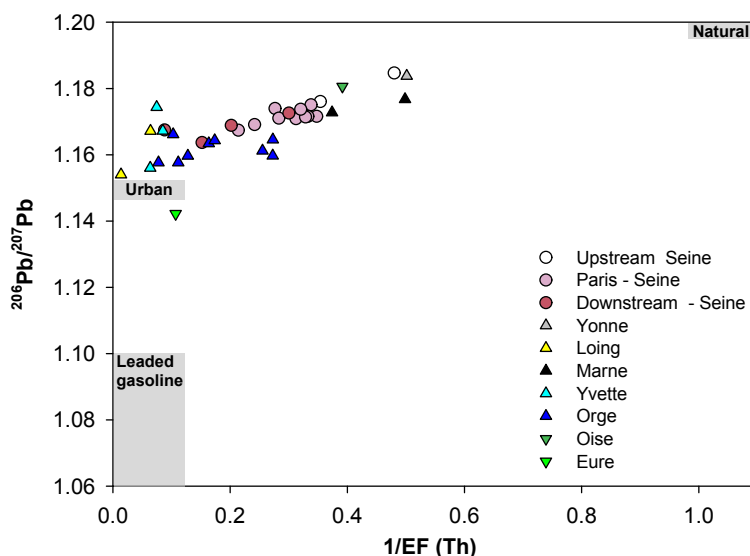


Figure 5. $^{207}\text{Pb}/^{206}\text{Pb}$ vs $1/\text{EF}$ in the sediment collected in the Seine River and its tributaries (uncertainty on $^{207}\text{Pb}/^{206}\text{Pb}$ ratio determination $\leq 0.5\%$). Potential Pb sources, represented with grey boxes showing the variability of their $^{208}\text{Pb}/^{207}\text{Pb}$ ratio, include natural lead (Elbaz-Poulichet et al., 1986), urban lead (Ayrault et al., 2012) and leaded gasoline (Véron et al., 1999).

3.4 Correlations, PCA and Enrichment Factors using the sediment dataset

3.4.1 Correlations and PCA

A correlation analysis was conducted using the sediment major elemental and thorium concentrations (Table 1). When analyzing those elements often used to correct data from potential particle size effects, a significant correlation was observed between Al and Th ($r=0.72$) while correlations between Ti and Al ($r=0.51$) and those between Ti and Th ($r=0.30$) were less significant. Considering those correlation values > 0.65 , Mn was the element that showed the most significant correlations (Mn and Th, $r=0.68$; Mn and Mg, $r= 0.79$; Mn an Al, $r=0.87$, Mn and Fe, $r=0.80$) while Na displayed only a significant correlation with Ca ($r=0.80$).

Table 1. Spearman correlation matrix for major and thorium concentrations.

	Th	Na	Mg	Al	K	Ca	Ti	Mn	Fe
Th	1.00	0.16	0.55***	0.72***	0.38*	0.13	0.30	0.68***	0.50**
Na		1.00	0.17	0.017	0.44*	0.80***	0.51***	0.11	0.22
Mg			1.00	0.77***	0.38	0.33	0.34*	0.79***	0.67***
Al				1.00	0.50***	0.29	0.51***	0.87***	0.84***
K					1.00	0.76***	0.93***	0.32	0.30
Ca						1.00	0.80***	0.12	0.082
Ti							1.00	0.29	0.29
Mn								1.00	0.80***
Fe									1.00

* p-value <0.05 ; ** p-value <0.001 ; *** p-value <0.0001

A PCA was performed on the radionuclide concentrations, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and metal concentrations measured on the sediment samples ($n=29$) (Figure 6). As Ti was not measured for those sediment samples collected in the Orge River, this element was removed from further analysis. Data were normalized to Th to remove potential particle size effects. The first component (F1) accounted for 51.4% of the total variance, compared to 13.8% and 8.5% for the second and third components, respectively. Three pools of parameters were discriminated based on this PCA: the first group (As, Ti, Fe, Al, Ni, Cr, Mg) was characterized by positive F1 and F2 components, the second group (Ag, Zn, Cu, Cd, K, Sb, Pb, $^{206}\text{Pb}/^{207}\text{Pb}$ and Na) was described by a positive F1 component and a negative F2 component, whereas the third group (Ca, ^{137}Cs , ^7Be) was represented by negative F1 and F2 components. The Orge (17, 18, 19) and the Loing sediment (24) samples were discriminated from the other samples by a positive correlation with the F1 component.

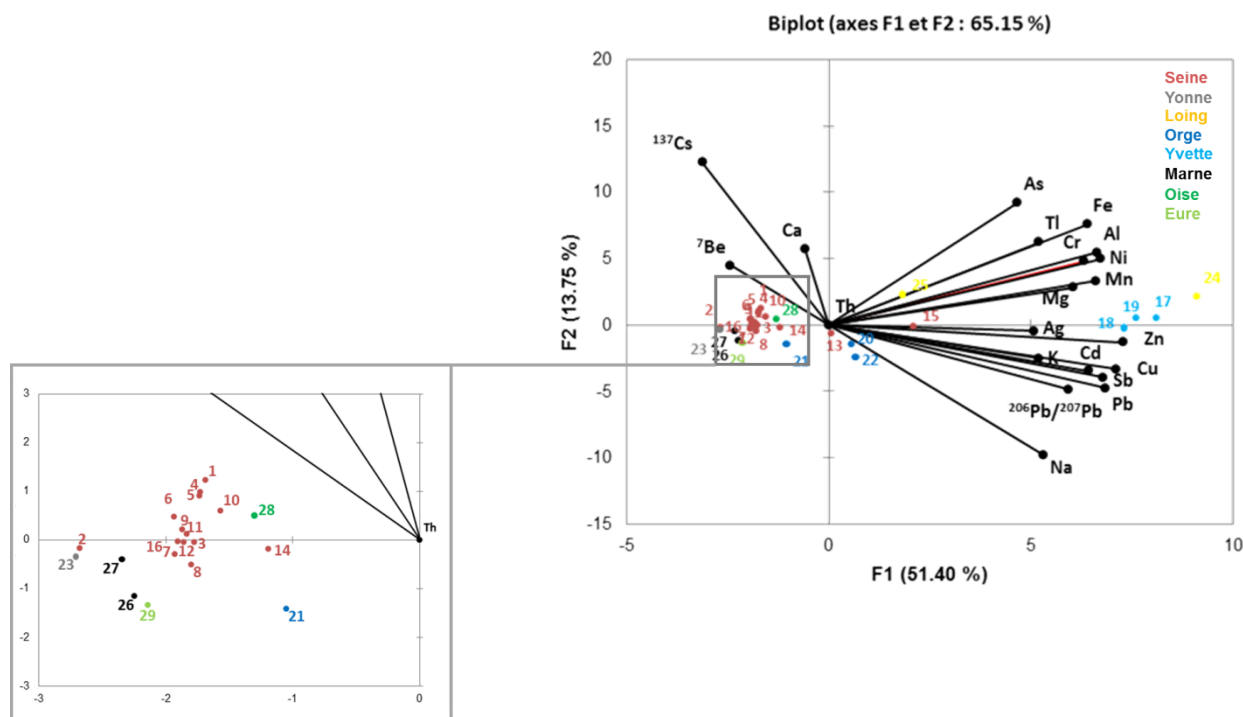


Figure 6. Results of the Principal Component Analysis performed on the sediment samples dataset (elemental and radionuclide concentrations, $^{206}\text{Pb}/^{207}\text{Pb}$ ratio) normalized to Th.

3.4.2 Enrichment Factors

Enrichment factors (EF) were calculated to discriminate between the natural and anthropogenic sources of metals/metalloids transported with sediment during the Seine River flood event (Figure 7).

For all the sediment collected along the Seine River and its tributaries, the following ranges of values were obtained using Th normalization: $1.2 < \text{EF}(\text{Cr}) < 7.6$, $1.1 < \text{EF}(\text{Ni}) < 6.3$, $2.1 < \text{EF}(\text{Zn}) < 19.1$, $2.1 < \text{EF}(\text{Cu}) < 26.5$, $0.9 < \text{EF}(\text{As}) < 6.8$, $1.8 < \text{EF}(\text{Cd}) < 23.8$, $1.2 < \text{EF}(\text{Sb}) < 19.8$, $1.7 < \text{EF}(\text{Pb}) < 72.4$ (Table S5). The highest EFs were observed for Pb, Cd, Sb and Zn. When normalized to Al, very similar trends although lower values were obtained (Table S5), with the highest EFs observed for Pb, Cd, Sb and Zn (Table S6, Figure S1).

For each element/normalization, the highest EFs were systematically found in the sediment collected in the Loing and Yvette Rivers. The lowest factors were observed in sediment collected in Paris and its vicinity while downstream of Paris, sediment collected to Bouafle, in the Seine River (15), exhibited higher EFs for Zn, Cu, Cd, Sb and Pb. For As, although the highest EFs were observed in sediment collected in the Loing River (24, 25), this element exhibited a different trend

with higher EFs in Paris and its vicinity ($1.6 < EF(As/Th) < 2$) compared to those values found in the Yvette (17, 18, 19) and Orge (20, 21, 22) Rivers ($1 < EF(As/Th) < 1.4$).

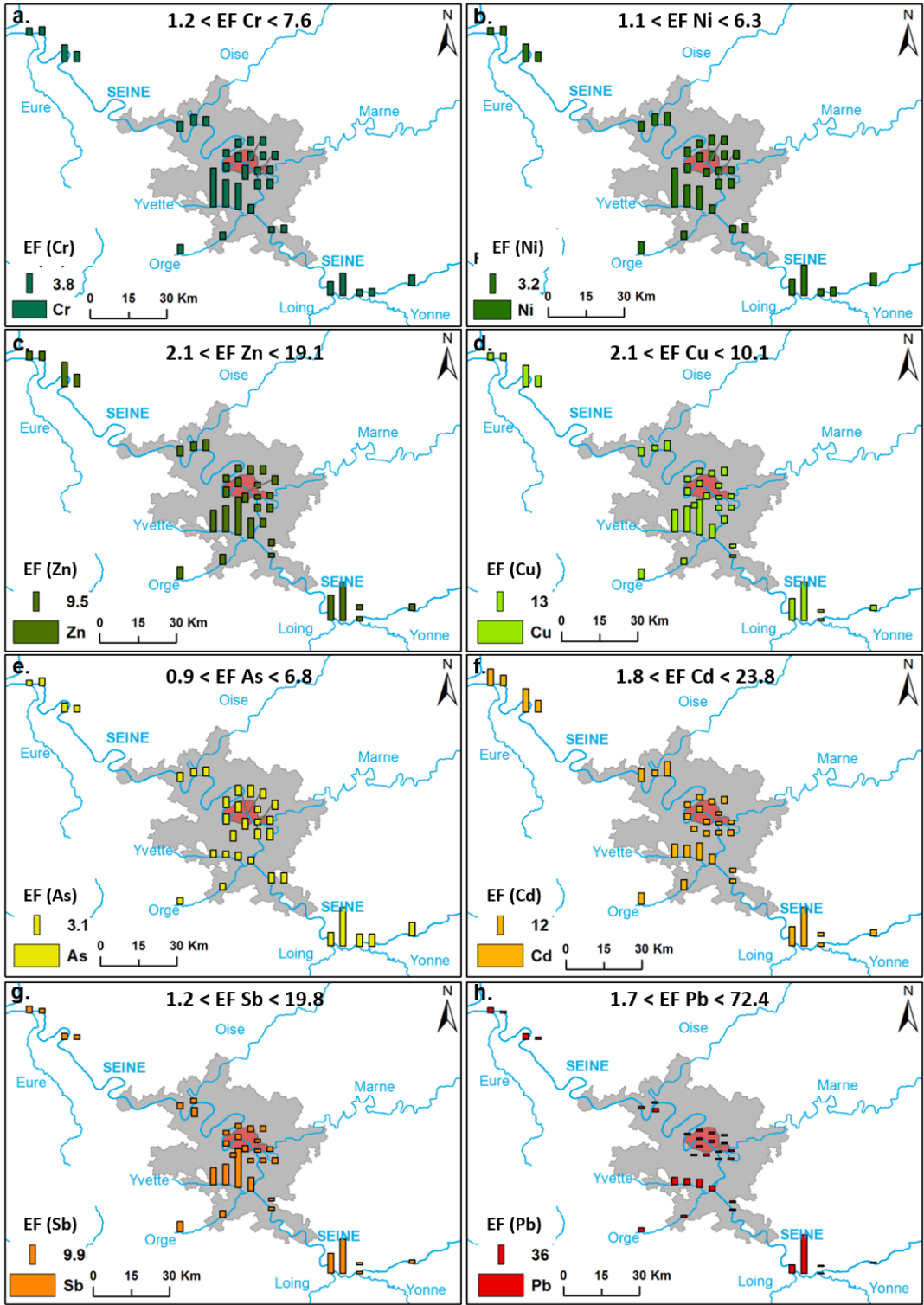


Figure 7. Enrichment Factors (EF) for Cr, Ni, Zn, Cu, As, Cd, Sb and Pb calculated for each sediment sample collected along the Seine River and its main tributaries. EFs were calculated after Th normalization.

4 Discussion

4.1 Particle size effect, normalization and carrier phases

Metal and radionuclide concentrations need to be normalized to limit potential particle size effects and provide meaningful interpretations of sediment contamination levels. Al, Ti, and Si are commonly used to this end in the literature (Bouchez et al., 2011; Grosbois et al., 2012; Quevauviller, 1989)). Although Th normalization was shown to be effective in a lowland river basin of France and in the Seine River basin (Le Cloarec et al., 2011; Foucher et al., 2015), this parameter is rarely used to this end. An inter-element correlation matrix was therefore used to identify those alternative elements that may be used to correct sediment data from potential particle size effects.

Ti was poorly correlated to Al and Th (section 3.4.1). Moreover, in urban catchments, the potential release of TiO_2 originating from paint and personal care products into the environment may prevent its use as a conservative element. In the current research, a significant correlation was observed between Th and Al ($r=0.72$), suggesting that both elements are able to correct sediment metal concentration from potential particle size effects. Al is a conservative element characteristic of the fine sediment fraction and it is commonly used as a grain-size proxy to limit the dilution by quartz, silica or calcite (Owens et al., 2005). Th is known to be preferentially fixed to fine particles and can also be used for normalization (Le Cloarec et al., 2011; Foucher et al. 2015). Accordingly, EFs were calculated using both elements for normalization. EFs calculated with Th were systematically higher (mean:4.8, σ :6.3) than EFs calculated with Al (mean:2.3, σ :2.4) although similar trends were observed with the highest and lowest EFs observed for the same sediment samples when using both methods. Furthermore, Th was the only element available for the entire dataset (i.e. sediment from the flood event and previous samples (Gateuille, 2013) used to characterize the four end-members in the modelling approach). Accordingly, the following discussion was restricted to those results corrected with Th.

After normalization to Th, a PCA was performed on the sediment metal and radionuclide contents to better visualize correlations between elements and to examine in particular those elements that may act as carrier phases (Figure 6). Most of the parameters contributed to the first component. These parameters were scattered into two groups with respect to the second component (to which Cs-137, Be-7, Ca are contributing). The group with a negative load on the second component is composed of Ag, Zn, Cu, Pb, Cd and Sb that are well-known urban pollutants (Sutherland, 2000; Marcheselli et al., 2010; Bi et al., 2011).

The occurrence of K in this group demonstrates the need to conduct further investigations regarding the mineralogical phases carrying this element. In the second group, As, Tl, Cr and Ni plotted close to Fe, Al, Mg and Mn, indicating that As, Tl, Cr and Ni could be carried by aluminosilicates and/or Fe or Mn oxyhydroxides. Furthermore, low EFs were calculated for As, Ni, Cr and Tl, suggesting that there is no longer significant contamination in these three elements in the Seine River Basin. This is consistent with previous findings reported in the literature (Tl: Ayrault et al., 2010; other: Meybeck et al., 2016).

Trace urban elements Ag, Zn, Cd, Cu, Sb, Pb are well correlated ($r > 0.88$) (Table S7) indicating that they are likely supplied by the same sources. However, a lack of correlation between urban elements and those characteristics of the clay fraction and oxyhydroxides was observed, suggesting that other carrier species are involved. As shown by Le Pape et al. (2013, 2014) for Pb and Zn respectively, changes in particulate speciation were observed suggesting that different carrier phases may be associated to a given urban metal. Priadi et al. (2010) observed along the Seine River that metal speciation may vary in downstream direction depending on the urban pressure. Seasonal variations may also impact metal speciation with changes in contamination sources and/or sediment diagenesis. All these processes may explain the lack of association observed between urban metals and elements characteristic of aluminosilicates and/or (Fe, Mn) oxyhydroxides for the sediment collected during the Seine River flood.

Most sediment samples collected in the Seine River and its main tributaries plotted together and were associated with ^7Be , ^{137}Cs and to a lesser extent with Ca. ^7Be and ^{137}Cs are strongly fixed to fine particles (Taylor, 2012). These sediment samples may be carried by carbonate phases. This is consistent with the sedimentary nature of the Seine River basin that includes 78% of various carbonate rocks such as chalk and limestone (Meybeck, 1999). Accordingly, the F2 component tends to discriminate a natural source, suggesting that these sediment samples would originate from the erosion of carbonate soils, characteristic of the geological nature of the Seine River basin. The Orge (17, 18, 19) and the Loing sediment (24) samples were discriminated from the remaining samples while being correlated to urban elements. This is consistent with the high EFs calculated for these samples, suggesting a significant urban contamination. These results differ from previous findings obtained in the Orge subcatchment (Le Pape et al. 2011) which showed that Zn and Cd behave differently from the remaining urban elements (Ag, Cu, Sb, Pb) in suspended sediment collected in this river (Le Pape et al., 2011). This suggests that during the flood of the Seine River, Zn originated from a different source than during usual low-flow conditions. The flood sediment investigated in the current research may be representative of a past and historical contamination

compared to the present-day contamination of the Orge subcatchment investigated by Le Pape et al. (2011). This interpretation is confirmed by radionuclide measurements that demonstrated that sediment consisted of older remobilized particles in the Orge River.

4.2 Metal contamination, short-term perspective

Predicted No Effect Concentrations (PNECs) defining the toxicity of elements in the environment were compared to the sediment metal concentrations (Barjhoux et al., 2016). PNECs are determined by environmental institutions recognized at the European level. Ni, Zn, Cu and Pb concentrations exceeded PNEC values in sediment collected along the Seine River and its tributaries, highlighting the potential risk for the environment (Figure 4). Only the sediment sampled in uppermost sections of the Seine River had concentrations lower than the PNEC values. For Cd, sediment concentrations remained lower than the PNEC value of 1.8 mg kg⁻¹ with the exception of one sediment sample, collected in the downstream section of the Seine River in Bouafle (15), slightly exceeding this value with a Cd concentration of 1.9 mg kg⁻¹. For Cr, As and Sb, sediment concentrations remained lower than the PNEC values, suggesting the absence of an environmental toxicity.

In a review by Viers et al. (2009), mean concentrations of trace elements in suspended sediment of World Rivers were provided, with a compilation of concentrations found in both pristine and human-impacted rivers. Compared to this dataset, elemental concentrations of the Seine River sediment were lower for Cr, Ni, As and Sb although in the same range for Zn, Cu, Cd, Pd and Tl (Table 2). Elemental concentrations found in the Seine flood sediment were in good agreement with those found in the Elbe and Ebro rivers (Baborowski et al., 2012; Roig et al., 2016) in Europe. These analogies suggest similarities with other major rivers impacted by human activities. However, the direct comparison of elemental concentrations measured in different catchments is difficult and must be undertaken with much caution because different types of samples (i.e. suspended particles, riverbed sediments, sediment cores) may be collected in different basins, reflecting the contamination of different particle size fractions (i.e. bulk, <2 mm, <63 µm, <0.45 µm) during various hydrological conditions. Accordingly, the normalization of geochemical data to a conservative element is required to enable comparison between different datasets. However, identifying a universal conservative element is not straightforward (see section 3.4). Despite these difficulties, comparing sediment metal concentrations is essential for environmental authorities to estimate contamination levels and evaluate their impact on riverine environments.

It is important to note that elemental concentrations in sediment collected during snapshot campaigns may reflect spatial and temporal variations, even over a short temporal period.

535 Sampling lag deposits has the benefit to essentially integrate the falling limb of the hydrograph.
536 However, at the catchment scale, sediment may be characterized by a spatial variability that
537 depends on its physical, chemical and biological properties and potential for erosion (Haag et al.,
538 2001; Baborowski et al., 2012). Accordingly, the sediment contamination patterns along the Seine
539 River and its tributaries could be partly explained by the nature of the deposited flood sediment.
540 Further investigations are required to comprehensively examine this perspective.

541 Another parameter that could be considered is the distribution of the metal contamination related
542 to hydrological parameters of the flood for each sampling location. Unfortunately, due to its sudden
543 and exceptional character, accurate flow measurements were not available but upstream
544 tributaries of the Seine River, such as the Loing River, were characterized by return periods > 50
545 years compared to the Seine River in Paris with return periods estimated to 10-20 years,
546 suggesting that the sediment metal contamination depends on the temporality of the flood and the
547 spatial distribution of rainfall.

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Table 2. Worldwide average concentrations of trace elements (mg kg⁻¹) in sediment from major rivers of the world.

River	Sample	Reference	Al	Cr	Ni	Zn	Cu	As	Cd	Sb	Tl	Pb
Worldwide Rivers			87200	130	75	208	76	36	1.6	2.2	0.5	61
South American Rivers			91000	79	46	184	59	-	-	-	-	76
North American Rivers			83000	115	50	137	34	-	-	-	-	22
Asian Rivers (Russia)	Suspended sediment (<0.45 µm)	Viers et al. (2009)	71000	260	123	300	145	-	-	-	-	35
Asian Rivers (China)			95000	117	68	145	53	-	-	-	-	64
African Rivers			113000	130	78	130	53	-	-	-	-	46
European Rivers			61000	164	66	346	172	-	-	-	-	71
Upper Continental Crust	Rocks	Taylor & McLennan (1995)	80400	35	20	71	25	-	0.1	0.2	0.8	20
Parana River (Brazil)	Suspended sediment (<0.45 µm)	Campodonico et al. (2014)	17.9% (Al ₂ O ₃)	128	45	-	80	-	-	-	0.63	28
Uruguay River (Argentina)	River sediment (bulk)	Tatone et al. (2016)	-	19	16	85	55	-	-	-	-	13
Mississippi River (USA)	Suspended sediment	Horowitz et al. (2008)	54667	67	41	93	21	9	0.5	2.4	-	26
Mekong River (Asia)	Suspend sediment (<0.45 µm)	Cenci et al. (2004)	90000	39	25	-	-	18	-	-	-	-
Jiaozhou Bay (China)	River sediment (bulk)	Xu et al. (2017)	135000	69	-	65	24	8	0.2	-	-	20
Nile River (Egypt)	River sediment (bulk)	Badawy et al. (2017)	43360	173	48	74	-	1	0.3	0.2	-	-
Congo River (Congo)	Suspended sediment (<0.2 µm)	Dupré et al. (1996)	-	121	86	-	-	-	-	-	-	36
Elbe River (Germany)	Sediment core (upper layer, 0-5 cm, <2 mm)	Baborowski et al. (2012)	-	-	22	473	63	24	-	-	-	82
Ebro River (Portugal)	River sediment (bulk)	Roig et al. (2016)	-	36	14	87	22	6	0.3	-	-	17
PNEC values	Sediment	Barjhoux et al. (2016)	-	110	17	93	22	17	1.8	11.2	-	47
Seine River, June 2016 flood event	Sediment (<63 µm)	This study	12900-46890	16-75	8-34	69-402	14-90	2-14	0.3-1.9	0.4-3.2	0.2-0.9	15-214
Seine River basin, natural contents	Sediment	Le Cloarec et al. (2011) Thévenot et al. (2007)	36535	52	27	76	14	5.5	0.3	0.8	-	26

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4.3 Metal contamination, long-term perspective

In a longer time perspective, Cr, Zn, Cu, Cd, Sb, Pb, Ni and As concentrations measured in the sediment from the Orge River, and from the Seine River in Puteaux (12) and Vernouillet (14) may be compared to those measured in samples collected at the same locations or in their immediate vicinity (Priadi et al., 2011b; Le Pape et al., 2012) (Figure 4). As sediment was sieved to 63 μm , elemental concentrations are compared to those of suspended particulate matter (SPM) samples. For the Orge River, the sediment elemental concentrations from the June 2016 flood event were lower than those found in the SPM collected between June 2010, and April 2011 (Le Pape et al., 2012). For the Seine River, the sediment elemental concentrations were lower (for Cr, Ni, Zn, Cu, As, Cd, Pb in Puteaux (12) and Cr, Zn, Cu, As in Vernouillet (14)) or in the same range of variation (for Sb in Puteaux (12) and for Ni, Cd, Sb, Pb in Vernouillet (14)) than those measured in the SPM collected between December, 2008, and September, 2009, in Bougival, located a few kilometers downstream of Puteau and Triel, on the opposite bank of Vernouillet (Priadi et al., 2011b). This dataset demonstrates that elemental concentrations (Cr, Ni, Zn, Cu, As, Cd, Sb, Pb, As and Ti) measured in the sediment from the June 2016 flood event remained lower or similar to those monitored from 2003 to 2011 in the same areas. Despite local inputs, such as those from the Orge, Yvette and Loing tributaries, metal and metalloid signatures were significantly diluted in the Seine River during the 2016 flood event.

As the Seine River contamination has been well documented since the 1970s, trace element concentrations (especially Cd, Cu, Zn, Pb, known as effective urban tracers in the Seine catchment, e.g. Thévenot et al. 2007) measured in sediment from the June 2016 flood can be placed in an historical contamination perspective. Analyses carried out between 1974 and 2000 on sedimentary archives, SPM and flood deposit samples showed an overall decline of Cd, Cr, Cu, Ni, Pb and Zn contents (Horowitz et al., 1999; Meybeck et al., 2007), with the Ni values similar to the geochemical background. Similarly, metal concentrations in flood deposits collected between 1994 and 2000 along the Seine River and its main tributaries (Yonne, Marne, Oise) were higher compared to those measured in sediment from the June 2016 flood event, indicating the occurrence of a significant decontamination (Table 2) (Grosbois et al., 2006).

Table 3. Zn, Cu, Cd and Pb concentrations (mg kg⁻¹) measured in flood deposits collected between 1994 and 2000 (from Grosbois et al., 2006, median values presented here) and in the June 2016 sediment (median values for the Paris sediment).

	Zn	Cu	Cd	Pb
Paris (1994-2000)	280	69	1.0	110
Paris (June 2016)	188	33	0.3	51
Poses (1994-2000)	350	83	1.9	110
Poses (June 2016)	198	41	1.2	53

These results are consistent with the interpretation of the lead isotopic signatures measured in the June 2016 sediment and show an increasing gradient of urban contamination in a downstream direction across the Seine River catchment together with the progressive decontamination of the Seine River catchment through time. Indeed, the Bouafle sediment core, located in the downstream section of the Seine River, indicated that since the end of the 1990s, lead signatures evolved from an urban to a natural source end-member (Ayrault et al., 2012). The lead signatures measured in the sediment collected in Bouafle after the June 2016 flood were even higher than that measured in the uppermost layer of the sediment core, further supporting the occurrence of a strong decontamination trend.

Ag and Tl contents may also be compared to the historical records deduced from the Bouafle sediment core (Ayrault et al., 2010). The 2016 flood sediment collected at Bouafle had an Ag concentration of 2.0 mg kg⁻¹, lower than the 3.8 mg kg⁻¹ measured in the 2003 sediment layer (Figure 4i). The highest Ag sediment concentration in the 2016 flood was 3.95 mg kg⁻¹ in Conflans-St-Honorine (13) and was similar to the value found in the core in 2003. This suggests that in downstream sections of the Seine River, Ag contamination has decreased during the last 15 years despite the potential local supply of Ag contamination to the river network. The 'Seine Aval' wastewater treatment plant, located less than 10 km upstream of the Conflans-St-Honorine sampling location (13) treats ~ 70% of the wastewater of the Parisian agglomeration (SIAAP). Accordingly, the highest Ag concentration (3.95 mg kg⁻¹) measured at Conflans-St-Honorine (13) may be related to the release of treated wastewater upstream of the Seine-Oise confluence. For the Oise sediment, the Ag content only reached 0.26 mg kg⁻¹. Downstream of the Seine-Oise confluence, the Ag content in sediment decreased from 3.95 mg kg⁻¹ to 1.10 mg kg⁻¹, suggesting a dilution of the Ag sediment contamination by the Oise River sediment.

Once again, these findings highlight that the 'Seine Aval' wastewater treatment plant is a significant source of Ag contamination of the Seine River (Ayrault et al., 2010). Tl sediment concentrations, ranging between 0.20 and 0.96 mg kg⁻¹, remained in the same range of variations as those found in the Bouafle sediment core (0.66 to 1.01 mg kg⁻¹), demonstrating the absence of

specific TI contamination during the 2016 flood event compared to the TI records over the last 70 years, even in Paris where the highest TI concentrations were measured (Figure 4j). These data confirm the absence of TI contamination through the Seine catchment as reported by Tremel et al. (1997) and Ayrault et al. (2010).

As previously mentioned, the normalization of elemental concentrations to a conservative element, such as Th, is required to compare different geochemical datasets. Accordingly, EFs calculated for the June 2016, flood event were compared to those estimated for the contamination records reconstructed for the period 1943-2003 based on the analysis of the Bouafle sediment core (Le Cloarec et al., 2011) (Table 4). EFs were the highest between 1958 and 1960 due to the economic development following World War II. Then, EFs continuously decreased as a result of the evolution of industrial production processes, the implementation of wastewater treatment plants and environmental policies, leading to the progressive metal decontamination of the Seine River catchment. Mean EFs estimated for the June 2016, flood event in the Seine River were lower for Cr, Cu, As, Cd and in the same range of values for Zn, Sb and Pb than those estimated in sediment that deposited in Bouafle in 2003 (Le Cloarec et al., 2011) (Table 3). This indicated that despite the progressive decontamination of the Seine River, also observed in Meybeck et al. (2007) and Le Cloarec et al. (2011) from 1950 to 2005 and more recently in the urban Orge subcatchment from 2000 to 2010 (Le Pape et al. 2012), major flood events may remobilize and export contaminated material characterized by EFs similar to those obtained more than 10 years ago.

EFs of the sediment collected in the Seine tributaries reached even higher values than those calculated for the sediment that deposited in the 1950s and 1960s. This is the case for Sb and Pb, with the highest EFs estimated for the Yvette ($EF_{Sb}=19.8$) and Loing ($EF_{Pb}=72.4$) tributaries. These results suggest the contribution of local inputs of contaminated sediment to the Seine River. $^{206}Pb/^{207}Pb$ signatures may support this hypothesis. Accordingly, the urban signature of the Loing sediment is distinguishable from the remaining lead signatures. This tributary was strongly impacted by the June 2016 flood, with the highest water specific discharges and the most devastating effect. Local urban sources such as the overflowing from wastewater treatment plant may have contributed to this specific signature. In the same way, the Eure sediment exhibited the lowest isotopic signature, suggesting a strong anthropogenic contamination that may be attributed to elevated Pb concentrations in the Eure sediment due to the release of local industries (battery plant) as observed in previous studies (Meybeck et al., 2004; Chiffolleau and Sonke, 2012), corroborating the low $^{206}Pb/^{207}Pb$ signature measured in June 2016. The single use of elemental

concentrations did not highlight these results while EFs supported the investigation of contamination levels at the catchment scale, with the direct comparison of samples collected at different locations throughout time.

Table 4. EFs (Th normalization) estimated for the sediment from the June 2016 flood event and for the sediment from the Bouafle sediment core (Le Cloarec et al., 2011)

		EF (Cr)	EF (Ni)	EF (Zn)	EF (Cu)	EF (As)	EF (Cd)	EF (Sb)	EF (Pb)
June 2016 Seine River	Min	1.2	1.1	2.2	1.8	1.2	2.3	1.5	2.0
	Max	3.3	2.8	12.1	14.7	2.1	14.4	4.6	11.3
	Mean	1.7	1.6	4.6	4.9	1.7	4.8	2.6	4.0
June 2016 Seine tributaries	Min	1.3	1.1	2.1	1.6	0.9	1.8	1.2	1.7
	Max	7.6	6.3	19.1	26.5	6.8	23.8	19.8	72.4
	Mean	2.8	2.3	7.7	9.4	1.8	7.0	6.5	11.5
Bouafle sediment core	Min	2	-	5	6	3	9	3	4
	Max	7	-	29	41	6	188	15	29
	Surface layer	2	-	5	6	3	9	3	4

4.4 Sediment sources and metal contamination

The anthropogenic pressure of the June 2016 flood event was investigated using EFs to focus on the sediment metal contamination and radionuclides to examine the spatial variation of their sources. In upper catchment areas, the sediment from Bray-sur-Seine (01) mainly originated from the remobilization (59%) of subsurface (69%) sources. EFs were low and ranged between 1.7 for Sb and 3.7 for Cu. This sediment, collected upstream of the Yonne and Loing Rivers was not significantly affected by the June 2016 flood event and would be representative of the baseline Seine contamination level during low flow periods.

In the sediment collected in the Yonne and Loing tributaries, surface and subsurface sources were well balanced (mean surface contribution of $47 \pm 4\%$) with a strong remobilization of particles (mean value of $70 \pm 3\%$). EFs for the Yonne River sediment were systematically lower than 2.2, suggesting minimal or moderate pollution, with elemental concentrations reflecting the local geochemical background. In the Loing River, characterized by the highest water specific discharges, elevated EFs in Zn (19.1), As (6.8), Cd (23.8), Pb (72.4) were estimated for deposited sediment. Accordingly, depending on the element considered, the Loing River may be considered as significantly to extremely polluted. This extreme pollution may likely be related to the extensive flooding in this area, which was a 50 yr return interval event.

In the Orge and Yvette tributaries, sediment transported during the flood mainly consisted of remobilized subsurface material, relatively enriched in metals. These particles may have been eroded from channel banks following dam removal conducted in the Orge and Yvette catchments since 2010 in the context of the ecological remediation of water bodies. The removal of these structures, by increasing water velocity, facilitated the flush of the previously deposited particles, creating new erosion and deposition areas. The highest EFs in Cr (7.6), Ni (6.3) and Sb (19.8) were estimated for these two tributaries that can be characterized as significantly to highly polluted. Although Sb indicates the current contribution of urban contamination, this is not the case for Cr and Ni that likely originate from past industrial activities (1850-1950).

For sediment collected in Paris or in its vicinity, recently eroded surface sources dominated. This contribution may be explained by urban runoff, especially from parks and gardens. The second sediment source corresponds to the remobilization of particles originating both from the surface and the subsurface with varying contributions. EFs estimated for the Parisian sediment were low compared to those obtained in upstream tributaries such as the Loing, the Orge or the Yvette, with most of the EFs lower than 5, suggesting a moderate metal enrichment and pollution of the Seine River. Surprisingly, As and Tl peaks were observed for these sediment samples, suggesting the contribution of local sources, as their contents decreased again downstream of Paris.

For the Oise and Eure Rivers, the recently eroded surface contribution to the sediment was the highest. These two tributaries drain agricultural areas. Accordingly, the elevated contribution of surface particles may be explained by the erosion of agricultural soils, labelled with ^7Be from the rainfall of June 2016. These eroded particles, enriched in ^7Be , transited via the river network during the flood and likely settled during the falling limb. These trends were also observed for two sediment samples in the downstream section of the Seine River (14, 16). However, the contribution of local sources may be observed downstream of the Seine River (13, 15) with the supply of high proportions of remobilized subsurface particles. The local occurrence of channel bank collapse after the flood may explain these high subsurface contributions. EFs estimated for the downstream Seine River sediment were higher than those estimated in Paris, mainly for Zn, Cu, Cd, Pb, recognized as urban contamination tracers in the Seine catchment (Thévenot et al., 2007; Le Pape et al., 2012). These high EFs, ranging between 5.1 and 14.7, suggest that either contaminated particles were transported over long distances, down to Bouafle (15) where the meanders of the Seine River may allow particles to settle or previously deposited contaminated particles were remobilized.

Accordingly, even if the June 2016 flood event generated high amounts of sediment, trace element concentrations and EFs remained lower or in the same range of variations than those estimated in similar material during the last decades along the Seine River. It demonstrates the progressive decontamination of the Seine River sediment and the dilution effect of the flood, although local inputs of remobilized and highly contaminated sediment from tributaries may have occurred in some urban areas, particularly those that had the highest rainfall and discharges.

5 Conclusions

This study demonstrated the utility of collecting lag deposits to characterize the impact of a major flood event on the river sediment contamination and the utility of coupling radionuclides and elemental geochemistry to quantify sediment and contamination sources in highly urbanized catchments. During this event, an increase in metal contents was observed in a downstream direction with a high contaminant contribution from upper tributaries such as the Loing, Orge and Yvette Rivers characterized by urban signatures and corresponding to the remobilization of older sediment. In Paris and in downstream sections of the Seine River, the contribution of recently eroded particles to the sediment dominated with an increasing contribution from urban runoff in Paris and from the erosion of agricultural soils downstream of Paris.

Despite the exceptional nature of the flood, the sediment transiting the Seine River did not exhibit excessive contamination levels with most of the EFs indicative of moderate pollution, suggesting a dilution effect through the basin. Compared to historical records, the heavy metal contents of the sediment transported during the 2016 flood remained lower than those measured since the 1970s, reflecting the progressive metal decontamination ongoing in the Seine River basin. Even if the sediment metal contents are no longer characteristic of highly contaminated areas, Ni, Zn, Cu and Pb, sediment concentrations exceeded PNEC values. Accordingly, in the framework of Paris' candidacy to host the 2024 Summer Olympics with nautical competitions expected in the Seine River, attention should focus on the toxicity of these elements for the environment.

To discriminate specific mineralogical inputs related to this exceptional flood event, further investigations should be conducted to characterize the speciation of trace elements and their carrying phases. These findings could then be compared to those obtained in previous studies conducted on sediment collected during low-flow hydrological conditions. To improve the understanding of the impact of major flood events on sediment quality in urbanized basins such as the Seine River, continuous monitoring programs should be implemented. To ensure that water quality criteria are sufficient for events organized in the Seine River, attention should also focus

on the analysis of organic contaminants such as polycyclic aromatic hydrocarbons, polychlorobiphenyls or poly and perfluoroalkyl substances and microbial communities in sediment.

6 Acknowledgements

This work received financial support from the Seine-Normandie Water Agency (no 1065961 (1) 2016) and was conducted in the framework of PIREN-Seine long term environmental monitoring and research programs. The authors would like to thank Louise Bordier for technical assistance with ICP-MS measurements and Claire Froger for the urban runoff sampling.

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Supporting Information

Table S1. ^{137}Cs and ^7Be activities (Bq kg^{-1}) in sediment samples.

Sample	River	Localisation	Sampling date	Y (Lambert)	X (Lambert)	$^{137}\text{Cs} \pm 2\sigma$ (Bq kg^{-1})		$^7\text{Be} \pm 2\sigma$ (Bq kg^{-1})	
1	Seine	Bray-sur-Seine	06/06/2016	48.41761	3.23822	2.4	0.2	109.3	6.3
2	Seine	Corbeil-Essonnes	06/06/2016	48.60921	2.49017	3.3	0.2	93.7	5.4
3	Seine	Alfortville	06/06/2016	48.80571	2.41055	2.7	0.1	136.6	4.9
4	Seine	Ivry-sur-Seine	06/07/2016	48.79923	2.41441	5.5	0.4	144.8	6.2
5	Seine	Paris (Austerlitz station)	06/06/2016	48.84594	2.36331	5.2	0.5	176.1	8.1
6	Seine	Paris (Institut du Monde Arabe)	06/06/2016	48.84855	2.35869	4.9	0.3	112.7	4.7
7	Seine	Paris (Jussieu University)	06/06/2016	48.84937	2.35774	3.8	0.2	88.8	5.7
8	Seine	Paris (Notre-Dame)	06/06/2016	48.85051	2.35373	2.5	0.2	66.3	2.7
9	Seine	Paris (Orsay Museum)	06/06/2016	48.86035	2.32744	4.0	0.2	131.9	3.5
10	Seine	Paris (Pont AlexandreIII)	06/06/2016	48.86284	2.30478	4.9	0.2	135.4	3.4
11	Seine	Paris (Eiffel Tower)	06/06/2016	48.86074	2.29486	4.1	0.2	119.6	2.9
12	Seine	Puteaux	06/06/2016	48.87722	2.24565	3.9	0.1	94.1	4.8
13	Seine	Conflans St-Honorine	06/01/2016	48.98772	2.07451	2.0	0.1	91.4	3.4
14	Seine	Vernouillet	06/01/2016	48.96823	1.99838	3.6	0.2	96.7	5.3
15	Seine	Bouafle	09/28/2016	49.21123	1.37151	2.2	0.2	10.0	1.3
16	Seine	Poses	06/06/2016	49.30408	1.24755	3.5	0.2	227.3	7.3
17	Yvette	Orsay	06/06/2016	48.69970	2.17823	0.5	0.1	0.0	10.0
18	Yvette	Orsay	06/06/2016	48.69990	2.17799	0.4	0.1	12.1	3.4
19	Yvette	Longjumeau	06/06/2016	48.68976	2.31176	0.8	0.1	61.1	3.7
20	Orge	Dourdan	06/06/2016	48.53262	2.00159	0.6	0.1	8.5	0.9
21	Orge	Egry	06/06/2016	48.58490	2.22765	1.2	0.1	11.0	1.4
22	Orge	Viry-Châtillon	06/06/2016	48.67759	2.37896	0.0	0.5	24.2	3.0
23	Yonne	Montereau-Fault-Yonne	06/06/2016	48.38178	2.95801	3.8	0.2	91.1	5.3
24	Loing	Moret-sur-Loing	06/06/2016	48.38457	2.80530	0.6	0.1	0.0	9.6
25	Loing	Moret-sur-Loing	06/06/2016	48.38518	2.80378	4.3	0.2	79.0	4.8
26	Marne	Joinville-le-Pont	06/07/2016	48.81793	2.47020	2.0	0.2	64.2	2.4
27	Marne	Alfortville	06/06/2016	48.81588	2.41483	3.5	0.1	135.3	4.0
28	Oise	Conflans St-Honorine	06/06/2016	48.98899	2.07123	4.0	0.1	228.5	6.0
29	Eure	Léry-les-Damps	06/06/2016	49.30398	1.17749	3.2	0.2	215.5	8.9

13 **Table S2. Four end-members modelling results for each sediment sample.**

Sample	River	Localisation	Recently eroded subsurface (%)	Re-suspended subsurface (%)	Recently eroded surface (%)	Re-suspended surface (%)
1	Seine	Bray-sur-Seine	28 ± 13%	41 ± 5%	13 ± 13%	18 ± 9%
2	Seine	Corbeil-Essonnes	17 ± 18%	37 ± 8%	19 ± 19%	27 ± 13%
3	Seine	Alfortville	34 ± 17%	29 ± 7%	18 ± 9%	19 ± 9%
4	Seine	Ivry-sur-Seine	12 ± 10%	0 ± 5%	47 ± 13%	41 ± 14%
5	Seine	Paris (Austerlitz station)	9 ± 9%	0 ± 8%	64 ± 13%	27 ± 14%
6	Seine	Paris (Institut du Monde Arabe)	1 ± 14%	19 ± 6%	47 ± 15%	33 ± 10%
7	Seine	Paris (Jussieu University)	3 ± 13%	35 ± 17%	36 ± 25%	26 ± 8%
8	Seine	Paris (Notre-Dame)	5 ± 11%	58 ± 5%	21 ± 12%	16 ± 8%
9	Seine	Paris (Orsay Museum)	13 ± 11%	22 ± 5%	40 ± 12%	25 ± 8%
10	Seine	Paris (Pont AlexandreIII)	8 ± 30%	12 ± 11%	48 ± 34%	32 ± 16%
11	Seine	Paris (Eiffel Tower)	9 ± 29%	24 ± 12%	40 ± 33%	27 ± 19%
12	Seine	Puteaux	3 ± 29%	35 ± 12%	36 ± 33%	26 ± 19%
13	Seine	Conflans St-Honorine	16 ± 17%	55 ± 7%	19 ± 20%	10 ± 12%
14	Seine	Vernouillet	8 ± 3%	1 ± 38%	66 ± 44%	25 ± 15%
15	Seine	Bouafle	3 ± 1%	74 ± 2%	0 ± 1%	23 ± 2%
16	Seine	Poses	39 ± 3%	0 ± 1%	51 ± 1%	10 ± 3%
17	Yvette	Orsay	2 ± 39%	96 ± 1%	1 ± 51%	1 ± 6%
18	Yvette	Orsay	3 ± 3%	96 ± 4%	1 ± 1%	0 ± 1%
19	Yvette	Longjumeau	19 ± 4%	75 ± 1%	3 ± 3%	3 ± 2%
20	Orge	Dourdan	2 ± 2%	96 ± 2%	0 ± 2%	2 ± 2%
21	Orge	Egry	3 ± 3%	86 ± 2%	0 ± 3%	11 ± 3%
22	Orge	Viry-Châtillon	8 ± 1%	92 ± 1%	0 ± 1%	0 ± 1%
23	Yonne	Montereau-Fault-Yonne	32 ± 2%	24 ± 1%	0 ± 1%	44 ± 3%
24	Loing	Moret-sur-Loing	3 ± 2%	95 ± 1%	0 ± 1%	2 ± 1%
25	Loing	Moret-sur-Loing	27 ± 2%	22 ± 1%	0 ± 1%	51 ± 2%
26	Marne	Joinville-le-Pont	22 ± 1%	57 ± 1%	0 ± 1%	21 ± 2%
27	Marne	Alfortville	48 ± 6%	12 ± 2%	0 ± 6%	40 ± 4%
28	Oise	Conflans St-Honorine	12 ± 5%	4 ± 2%	84 ± 4%	0 ± 1%
29	Eure	Léry-les-Damps	24 ± 8%	12 ± 2%	64 ± 6%	0 ± 1%

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Table S3. Trace element concentrations (mg kg⁻¹) and lead isotope ratios (²⁰⁷Pb/²⁰⁶Pb) in the Seine River catchment sediment.

Sample	River	Localisation	Cr	Ni	Zn	Cu	As	Cd	Sb	Pb	Ag	Tl	Th	²⁰⁶ Pb/ ²⁰⁷ Pb
1	Seine	Bray-sur-Seine	29	16	69	14	3.2	0.3	0.4	15	0.10	0.26	3.4	1.1847 ± 0.0051
2	Seine	Corbeil-Essonnes	35	18	95	15	7.0	0.4	0.7	30	0.17	0.57	7.1	1.1834 ± 0.0044
3	Seine	Alfortville	40	19	152	33	6.9	0.5	1.1	45	0.38	0.61	5.9	1.1739 ± 0.0056
4	Seine	Ivry-sur-Seine	58	26	201	29	13.7	0.6	1.3	49	0.47	0.90	8.0	1.1716 ± 0.0031
5	Seine	Paris (Austerlitz station)	60	27	222	33	12.7	0.6	1.1	51	0.54	0.87	8.0	1.1716 ± 0.0017
6	Seine	Paris (Institut du Monde Arabe)	55	24	175	32	11.0	0.6	1.1	49	0.45	0.77	7.8	1.1751 ± 0.0025
7	Seine	Paris (Jussieu University)	46	23	159	34	9.4	0.6	1.1	53	0.60	0.71	7.3	1.1716 ± 0.0062
8	Seine	Paris (Notre-Dame)	36	15	158	28	7.4	0.5	1.1	50	0.36	0.46	5.7	1.1691 ± 0.0022
9	Seine	Paris (Orsay Museum)	49	21	193	33	10.8	0.6	1.3	49	0.58	0.66	7.2	1.1709 ± 0.0022
10	Seine	Paris (Pont Alexandre III)	56	25	240	43	11.3	0.7	1.3	57	0.70	0.76	7.6	1.1710 ± 0.0020
11	Seine	Paris (Eiffel Tower)	52	23	209	34	9.7	0.7	1.3	48	0.44	0.66	7.4	1.1714 ± 0.0042
12	Seine	Puteaux	45	25	156	33	9.1	0.6	1.1	47	1.81	0.67	7.2	1.1737 ± 0.0041
13	Seine	Conflans St-Honorine	35	22	156	35	4.8	1.0	1.4	64	3.95	0.36	4.6	1.1637 ± 0.0030
14	Seine	Vernouillet	53	23	218	47	8.3	1.3	1.4	72	1.10	0.63	6.9	1.1689 ± 0.0078
15	Seine	Bouafle	75	34	402	90	8.9	1.9	1.1	129	2.00	0.63	5.4	1.1674 ± 0.0066
16	Seine	Poses	52	24	198	41	6.5	1.2	1.2	53	0.93	0.52	7.5	1.1726 ± 0.0054
17	Yvette	Orsay	45	19	92	25	4.5	0.3	0.8	40	0.19	0.27	1.4	1.1744 ± 0.0053
18	Yvette	Orsay	34	12	121	30	4.1	0.3	1.0	37	0.33	0.30	1.5	1.1672 ± 0.0036
19	Yvette	Longjumeau	55	21	288	68	7.3	0.6	3.2	83	0.89	0.41	2.5	1.1560 ± 0.0123
20	Orge	Dourdan	16	9	78	16	2.5	0.4	0.7	26	0.07	0.25	2.1	1.1646 ± 0.0045
21	Orge	Egry	19	9	92	15	2.7	0.5	0.7	25	0.16	0.28	3.1	1.1618 ± 0.0039
22	Orge	Viry-Châtillon	18	8	152	28	2.4	0.3	1.1	52	0.46	0.22	2.5	1.1583 ± 0.0044
23	Yonne	Montereau-Fault-Yonne	43	21	113	15	10.8	0.4	0.6	35	0.24	0.89	8.2	1.1838 ± 0.0014
24	Loing	Moret-sur-Loing	26	15	165	42	10.2	0.8	1.6	214	0.20	0.20	1.4	1.1540 ± 0.0068
25	Loing	Moret-sur-Loing	44	23	300	67	11.3	1.1	2.6	129	0.63	0.49	3.9	1.1672 ± 0.0076
26	Marne	Joinville-le-Pont	38	15	115	23	5.4	0.4	1.0	36	0.18	0.31	6.3	1.1728 ± 0.0024
27	Marne	Alfortville	83	20	120	30	5.4	0.4	0.8	31	0.32	0.38	7.3	1.1768 ± 0.0089
28	Oise	Conflans St-Honorine	68	31	195	32	8.0	0.7	1.3	41	0.26	0.48	7.6	1.1806 ± 0.0059
29	Eure	Léry-les-Damps	47	21	212	43	4.8	1.9	1.8	156	0.67	0.35	7.9	1.1422 ± 0.0066
Geochemical background of the Seine River catchment (from Thévenot et al., 2007 and Le Cloarec et al., 2011)			52		76	14	5.5	0.3	<0.8	26			12	

27 **Table S4. Major element concentrations (mg kg⁻¹) in the Seine River catchment sediment.**

Sample	River	Localisation	Na	Mg	K	Ca	Ti	Mn	Fe
1	Seine	Bray-sur-Seine	962	2442	5174	247632	1160	299	11617
2	Seine	Corbeil-Essonnes	1373	3090	7756	183693	1938	488	17608
3	Seine	Alfortville	2040	3099	8512	155325	2046	384	17436
4	Seine	Ivry-sur-Seine	1483	4438	10690	147500	2640	676	27590
5	Seine	Paris (Austerlitz station)	1502	4530	11000	131100	2544	629	28010
6	Seine	Paris (Institut du Monde Arabe)	1721	4223	10570	141200	2594	552	25740
7	Seine	Paris (Jussieu University)	1904	3989	8606	143456	2155	506	20866
8	Seine	Paris (Notre-Dame)	1712	3025	8477	144500	1758	406	16700
9	Seine	Paris (Orsay Museum)	1816	3852	9581	148800	2337	519	22760
10	Seine	Paris (Pont AlexandreIII)	1650	4403	10210	140200	2550	585	26750
11	Seine	Paris (Eiffel Tower)	1899	4028	9750	139000	2377	543	23650
12	Seine	Puteaux	1751	3355	8507	158586	2051	465	19322
13	Seine	Conflans St-Honorine	2099	3024	6927	167354	1575	330	13238
14	Seine	Vernouillet	2002	4287	8623	154057	1956	477	21258
15	Seine	Bouafle	2895	4653	1890	142709	1796	653	26469
16	Seine	Poses	2689	3995	9074	135074	2059	589	20192
17	Yvette	Orsay	5261	1586	10884	14486	2930	285	11958
18	Yvette	Orsay	5352	1829	11071	16628	2684	283	12700
19	Yvette	Longjumeau	4838	4197	11742	35341	2883	471	22677
20	Orge	Dourdan	1972	1501	6504	23959	-	189	7306
21	Orge	Egry	1787	1378	8786	18912	-	251	7815
22	Orge	Viry-Châtillon	1462	1495	7600	21099	-	279	7613
23	Yonne	Montereau-Fault-Yonne	1454	3082	9436	168960	2015	475	18755
24	Loing	Moret-sur-Loing	693	1395	2418	282077	704	248	23055
25	Loing	Moret-sur-Loing	945	2650	5588,3	181317	1775	436	23097
26	Marne	Joinville-le-Pont	2556	4311	8846	132300	2257	382	17400
27	Marne	Alfortville	2987	4577	9864	104536	2266	417	19575
28	Oise	Conflans St-Honorine	3109	5621	12314	73848	2561	1052	31845
29	Eure	Léry-les-Damps	3910	2798	8957	65268	2359	380	18339

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42 **Table S5. Enrichment Factor values for each sediment sample (Th normalization).**

Sample	River	Localisation	Cr	Ni	Zn	Cu	As	Cd	Sb	Pb
1	Seine	Bray-sur-Seine	2.0	2.1	3.3	3.7	2.1	3.9	1.7	2.1
2	Seine	Corbeil-Essonnes	1.2	1.1	2.2	1.8	1.7	2.3	1.5	2.0
3	Seine	Alfortville	1.6	1.5	4.2	4.9	1.6	3.5	3.0	3.6
4	Seine	Ivry-sur-Seine	1.7	1.5	4.1	3.1	2.0	2.9	2.5	2.9
5	Seine	Paris (Austerlitz station)	1.8	1.5	4.5	3.6	1.8	3.1	2.2	3.0
6	Seine	Paris (Institut du Monde Arabe)	1.7	1.4	3.6	3.6	1.7	3.1	2.3	3.0
7	Seine	Paris (Jussieu University)	1.5	1.4	3.5	4.1	1.8	3.3	2.3	3.5
8	Seine	Paris (Notre-Dame)	1.5	1.2	4.5	4.3	1.9	3.3	2.8	4.1
9	Seine	Paris (Orsay Museum)	1.6	1.4	4.3	4.0	2.0	3.3	2.8	3.2
10	Seine	Paris (Pont AlexandreIII)	1.7	1.5	5.1	5.0	1.8	3.6	2.6	3.5
11	Seine	Paris (Eiffel Tower)	1.7	1.4	4.6	4.0	1.8	3.8	2.7	3.0
12	Seine	Puteaux	1.5	1.6	3.5	4.1	1.8	3.2	2.3	3.1
13	Seine	Conflans St-Honorine	1.8	2.2	5.5	6.8	1.6	8.8	4.6	6.6
14	Seine	Vernouillet	1.8	1.5	5.1	6.0	1.6	7.8	3.1	5.0
15	Seine	Bouafle	3.3	2.8	12.1	14.7	1.7	14.4	3.2	11.3
16	Seine	Poses	1.7	1.5	4.3	4.8	1.4	6.5	2.4	3.3
17	Yvette	Orsay	5.3	3.6	13.1	17.6	1.1	7.4	10.5	11.7
18	Yvette	Orsay	7.6	6.3	10.6	15.5	1.3	8.1	8.7	13.4
19	Yvette	Longjumeau	5.2	3.8	18.7	24.0	1.4	10.5	19.8	15.7
20	Orge	Dourdan	1.9	2.0	6.0	6.7	1.2	7.1	5.3	7.2
21	Orge	Egly	1.4	1.3	4.8	4.2	1.1	6.1	3.4	3.8
22	Orge	Viry-Châtillon	1.7	1.4	9.8	9.7	1.2	5.7	6.9	9.9
23	Yonne	Montereau-Fault-Yonne	1.3	1.2	2.2	1.6	2.2	2.2	1.2	2.0
24	Loing	Moret-sur-Loing	4.4	5.0	19.1	26.5	6.8	23.8	17.7	72.4
25	Loing	Moret-sur-Loing	2.7	2.7	12.5	15.0	2.3	11.8	10.2	15.6
26	Marne	Joinville-le-Pont	1.4	1.1	2.9	3.2	1.4	2.5	2.5	2.7
27	Marne	Alfortville	1.4	1.1	2.1	2.7	1.0	1.8	1.6	1.7
28	Oise	Conflans St-Honorine	2.1	1.8	4.2	3.7	1.3	3.6	2.6	2.6
29	Eure	Léry-les-Damps	1.4	1.2	4.3	4.8	0.9	10.1	3.4	9.3

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54 **Table S6. Enrichment Factor values for each sediment sample (Al normalization).**

Sample	River	Localisation	Cr	Ni	Zn	Cu	As	Cd	Sb	Pb
1	Seine	Bray-sur-Seine	0,99	1,0	1,6	1,8	1,0	1,9	0,8	1,0
2	Seine	Corbeil-Essonnes	0,92	0,9	1,7	1,5	1,7	1,8	1,2	1,6
3	Seine	Alfortville	0,95	0,9	2,5	3,0	1,6	2,1	1,8	2,2
4	Seine	Ivry-sur-Seine	0,89	0,8	2,1	1,6	2,0	1,5	1,3	1,5
5	Seine	Paris (Austerlitz station)	0,90	0,8	2,3	1,8	1,8	1,6	1,1	1,5
6	Seine	Paris (Institut du Monde Arabe)	0,92	0,8	2,0	2,0	1,7	1,7	1,2	1,6
7	Seine	Paris (Jussieu University)	0,93	0,9	2,2	2,6	1,8	2,1	1,4	2,2
8	Seine	Paris (Notre-Dame)	0,98	0,8	3,0	2,8	1,9	2,2	1,9	2,7
9	Seine	Paris (Orsay Museum)	0,97	0,8	2,6	2,4	2,0	2,0	1,7	1,9
10	Seine	Paris (Pont AlexandreIII)	0,94	0,8	2,8	2,7	1,8	2,0	1,4	1,9
11	Seine	Paris (Eiffel Tower)	1,01	0,8	2,7	2,4	1,8	2,3	1,6	1,8
12	Seine	Puteaux	0,96	1,0	2,3	2,7	1,8	2,1	1,5	2,0
13	Seine	Conflans St-Honorine	1,22	1,5	3,7	4,6	1,6	6,0	3,1	4,5
14	Seine	Vernouillet	1,09	0,9	3,1	3,6	1,6	4,6	1,9	3,0
15	Seine	Bouafle	1,48	1,3	5,4	6,6	1,7	6,5	1,5	5,1
16	Seine	Poses	1,16	1,0	3,0	3,4	1,4	4,6	1,7	2,3
17	Yvette	Orsay	0,92	0,6	2,3	3,1	1,1	1,3	1,8	2,0
18	Yvette	Orsay	1,34	1,1	1,9	2,7	1,3	1,4	1,5	2,4
19	Yvette	Longjumeau	1,11	0,8	4,0	5,1	1,4	2,3	4,2	3,4
20	Orge	Dourdan	0,90	0,9	2,7	3,1	1,2	3,2	2,4	3,4
21	Orge	Egly	0,80	0,7	2,8	2,4	1,1	3,5	1,9	6,4
22	Orge	Viry-Châtillon	0,90	0,8	5,4	5,4	1,2	3,2	3,8	2,8
23	Yonne	Montereau-Fault-Yonne	0,93	0,9	1,7	1,2	2,2	1,6	0,9	1,5
24	Loing	Moret-sur-Loing	1,83	2,1	8,0	11,1	6,8	10,0	7,4	30,3
25	Loing	Moret-sur-Loing	0,95	1,0	4,5	5,4	2,3	4,2	3,7	5,6
26	Marne	Joinville-le-Pont	1,01	0,8	2,1	2,2	1,4	1,8	1,8	1,9
27	Marne	Alfortville	0,97	0,8	1,5	1,9	1,0	1,3	1,1	1,2
28	Oise	Conflans St-Honorine	1,13	1,0	2,2	2,0	1,3	1,9	1,4	1,4
29	Eure	Léry-les-Damps	0,98	0,8	3,0	3,3	0,9	6,9	2,4	6,4

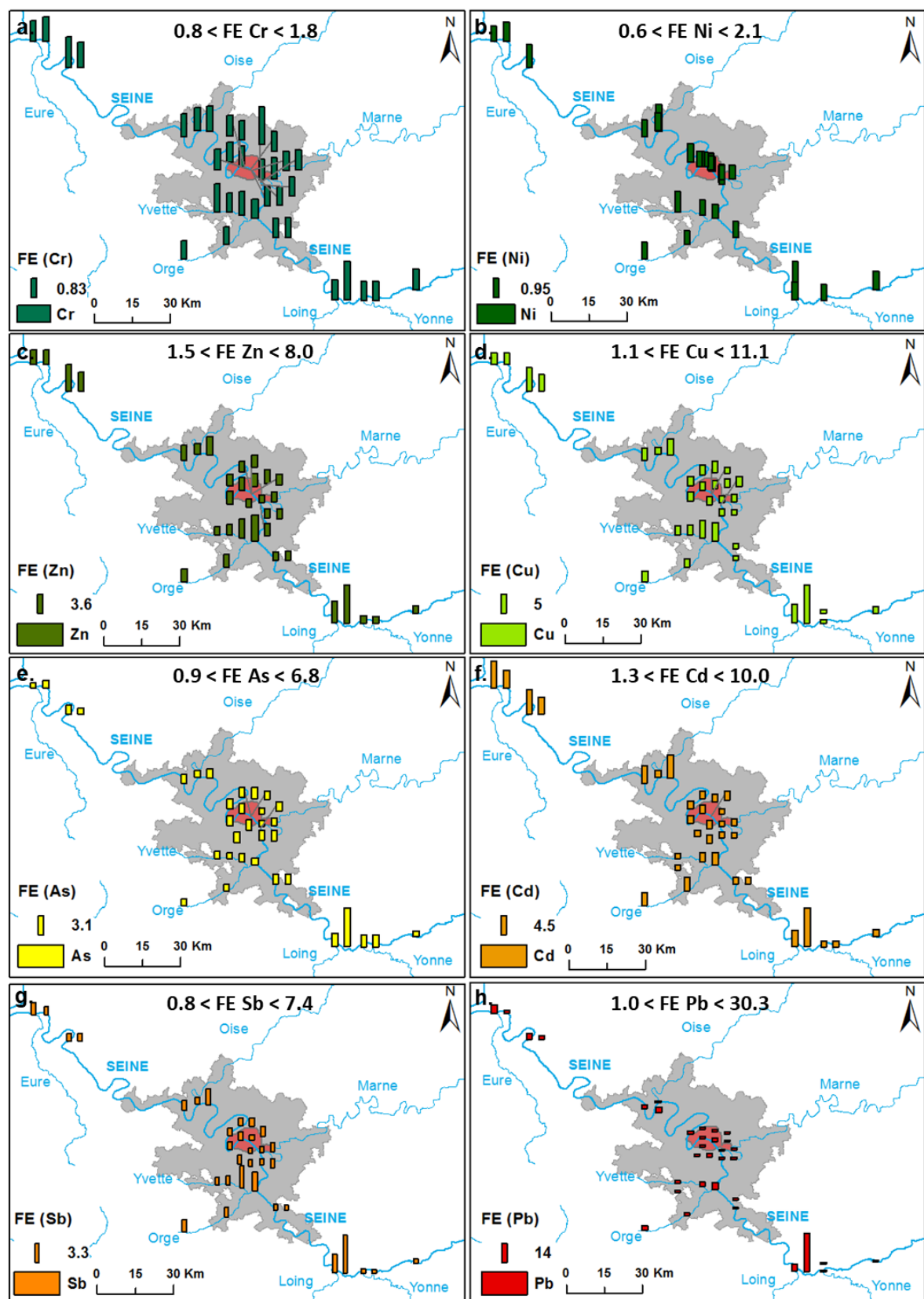


Figure S1. Enrichments Factors (EF) for Cr, Ni, Zn, Cu, As, Cd, Sb and Pb calculated for each sediment sample collected along the Seine River and its main tributaries. EFs were calculated after Al normalization.

60 **Table S7. Spearman correlation matrix for elemental concentration normalized to Th concentrations**

	Cr	Ni	Zn	Cu	As	Cd	Sb	Pb	Ag	Tl	²⁰⁶ Pb/ ²⁰⁷ Pb	Na	Mg	Al	K	Ca	¹³⁷ Cs	⁷ Be
Cr	1	0.840	0.647	0.609	0.514	0.544	0.509	0.483	0.447	0.497	0.505	0.472	0.889	0.801	0.547	-0.023	-0.055	-0.030
Ni	0.840	1	0.703	0.709	0.584	0.673	0.588	0.616	0.622	0.629	0.552	0.414	0.763	0.815	0.496	0.107	-0.053	-0.048
Zn	0.647	0.703	1	0.923	0.542	0.867	0.913	0.916	0.705	0.582	0.620	0.586	0.570	0.708	0.520	-0.094	-0.376	-0.286
Cu	0.609	0.709	0.923	1	0.405	0.888	0.903	0.954	0.764	0.507	0.695	0.685	0.546	0.605	0.484	-0.026	-0.468	-0.250
As	0.514	0.584	0.542	0.405	1	0.279	0.378	0.444	0.411	0.880	0.200	-0.074	0.411	0.667	0.198	0.169	0.144	-0.281
Cd	0.544	0.673	0.867	0.888	0.279	1	0.875	0.883	0.671	0.324	0.578	0.653	0.481	0.541	0.358	-0.012	-0.372	-0.128
Sb	0.509	0.588	0.913	0.903	0.378	0.875	1	0.936	0.634	0.448	0.692	0.709	0.489	0.586	0.583	-0.137	-0.531	-0.269
Pb	0.483	0.616	0.916	0.954	0.444	0.883	0.936	1	0.767	0.528	0.644	0.638	0.431	0.565	0.432	-0.038	-0.489	-0.310
Ag	0.447	0.622	0.705	0.764	0.411	0.671	0.634	0.767	1	0.382	0.344	0.359	0.327	0.372	0.103	0.085	-0.182	-0.066
Tl	0.497	0.629	0.582	0.507	0.880	0.324	0.448	0.528	0.382	1	0.366	0.101	0.400	0.733	0.311	0.041	-0.082	-0.403
²⁰⁶ Pb/ ²⁰⁷ Pb	0.505	0.552	0.620	0.695	0.200	0.578	0.692	0.644	0.344	0.366	1	0.721	0.593	0.555	0.706	0.109	-0.568	-0.465
Na	0.472	0.414	0.586	0.685	-0.074	0.653	0.709	0.638	0.359	0.101	0.721	1	0.544	0.376	0.612	-0.383	-0.813	-0.319
Mg	0.889	0.763	0.570	0.546	0.411	0.481	0.489	0.431	0.327	0.400	0.593	0.544	1	0.722	0.600	0.018	-0.232	-0.147
Al	0.801	0.815	0.708	0.605	0.667	0.541	0.586	0.565	0.372	0.733	0.555	0.376	0.722	1	0.608	-0.117	-0.053	-0.189
K	0.547	0.496	0.520	0.484	0.198	0.358	0.583	0.432	0.103	0.311	0.706	0.612	0.600	0.608	1	-0.290	-0.404	-0.161
Ca	-0.023	0.107	-0.094	-0.026	0.169	-0.012	-0.137	-0.038	0.085	0.041	0.109	-0.383	0.018	-0.117	-0.290	1	0.353	0.035
¹³⁷ Cs	-0.055	-0.053	-0.376	-0.468	0.144	-0.372	-0.531	-0.489	-0.182	-0.082	-0.568	-0.813	-0.232	-0.053	-0.404	0.353	1	0.537
⁷ Be	-0.030	-0.048	-0.286	-0.250	-0.281	-0.128	-0.269	-0.310	-0.066	-0.403	-0.465	-0.319	-0.147	-0.189	-0.161	0.035	0.537	1



Sediment deposit



Sources ?

Radionuclide measurements (^{137}Cs , ^7Be)
Spatial sources (surface vs subsurface)
Temporal dynamics (recent vs remobilized)

Metal contamination ?

Focus on Cr, Ni, Zn, Cu, As, Cd, Sb, Pb, Ag, Tl
Urban pressure ($^{206}\text{Pb}/^{207}\text{Pb}$)